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(54) Title: SUBSTITUTED PYRIDYL AMINE LIGANDS, COMPLEXES, CATALYSTS AND PROCESSES FOR POLYMER-  
IZING AND POLYMERS

(57) Abstract: New ligands, compositions, metal-ligand complexes and arrays with pyridylamine ligands are disclosed that catalyze the polymerization of monomers into polymers. Certain of these catalysts with hafnium metal centers have high performance characteristics, including higher comonomer incorporation into ethylene/olefin copolymers, where such olefins are for example, 1-octene, isobutylene or styrene. Certain of the catalysts are particularly effective at polymerizing propylene to high molecular weight isotactic polypropylene in a solution process at a variety of polymerization conditions.

5           **SUBSTITUTED PYRIDYL AMINE LIGANDS,  
COMPLEXES, CATALYSTS AND PROCESSES FOR  
POLYMERIZING AND POLYMERS**

10   **[0001]** This application claims the benefit of U.S. Provisional Patent Application No. 60/246,781, filed November 7, 2000 and the benefit of U.S. Provisional Patent Application No. 60/301,666, filed June 28, 2001, both of which are incorporated herein by reference for all purposes.

15                                   **FIELD OF THE INVENTION**

**[0002]** The present invention relates to ligands, complexes, compositions and/or catalysts that provide enhanced olefin polymerization capabilities based on a substituted pyridyl amine structure and hafnium. The invention also relates to methods of  
20   polymerization. The invention also relates to isotactic polypropylene and methods of preparing isotactic polypropylene.

**BACKGROUND OF THE INVENTION**

25   **[0003]** Ancillary (or spectator) ligand-metal coordination complexes (*e.g.*, organometallic complexes) and compositions are useful as catalysts, additives, stoichiometric reagents, monomers, solid state precursors, therapeutic reagents and drugs. Ancillary ligand-metal coordination complexes of this type can be prepared by combining an ancillary ligand with a suitable metal compound or metal precursor in a  
30   suitable solvent at a suitable temperature. The ancillary ligand contains functional groups that bind to the metal center(s), remain associated with the metal center(s), and therefore provide an opportunity to modify the steric, electronic and chemical properties of the active metal center(s) of the complex.

**[0004]** Certain known ancillary ligand-metal complexes and compositions are catalysts  
35   for reactions such as oxidation, reduction, hydrogenation, hydrosilylation,

hydrocyanation, hydroformylation, polymerization, carbonylation, isomerization, metathesis, carbon-hydrogen activation, carbon-halogen activation, cross-coupling, Friedel-Crafts acylation and alkylation, hydration, dimerization, trimerization, oligomerization, Diels-Alder reactions and other transformations.

5 [0005] One example of the use of these types of ancillary ligand-metal complexes and compositions is in the field of polymerization catalysis. In connection with single site catalysis, the ancillary ligand typically offers opportunities to modify the electronic and/or steric environment surrounding an active metal center. This allows the ancillary ligand to assist in the creation of possibly different polymers. Group 4 metallocene  
10 based single site catalysts are generally known for polymerization reactions. See, generally, "Chemistry of Cationic Dicyclopentadienyl Group 4 Metal-Alkyl Complexes", Jordan, *Adv. Organometallic Chem.*, 1991, Vol. 32, pp. 325-153 and "Stereospecific Olefin Polymerization with Chiral Metallocene Catalysts", Brintzinger, et al., *Angew. Chem. Int. Ed. Engl.*, 1995, Vol. 34, pp. 1143-1170, and the references  
15 therein, all of which is incorporated herein by reference.

[0006] However, those of skill in the art of single site catalysis appreciate that there may be substantial differences in performance between different metal centers. For example, U.S. Patent 5,064,802 discloses a broad category of mono-cyclopentadienyl ligand catalysts with a broad disclosure of useful metals, and U.S. Patent 5,631,391 more  
20 specifically discloses that titanium metal centers offer performance advantages with respect to the same or similar ligands. Additionally, Coates, et al., *Angew. Chem. Int. Ed.*, 2000, vol. 39, pp. 3626-3629 describes the unpredictable nature of olefin polymerization catalyst structure-activity relationships. Thus, references that describe, for example, groups 3-13 and the lanthanides, for example in U.S. Patent 6,103,657, are  
25 not of adequate performance indicators of all that is within the scope of what is allegedly described. Moreover, as those of skill in the art appreciate, differences in ligand substituents typically polymerize different monomers at different performances under different polymerization conditions, and discovering those specifics remains a challenge.

[0007] One application for metallocene catalysts is producing isotactic polypropylene.  
30 An extensive body of scientific literature examines catalyst structures, mechanism and polymers prepared by metallocene catalysts. See, e.g., Resconi et al., "Selectivity in Propene Polymerization with Metallocene Catalysts," *Chem. Rev.* 2000, 100, 1253-1345 and G.W. Coates, "Precise Control of Polyolefin Stereochemistry Using Single-Site

Metal Catalysts," *Chem. Rev.* 2000, 100, 1223-1252 and the references cited in these review articles. See also, U.S. Patent 5,026,798 that reports a mono-cyclopentadienyl metallocene for the production of isotactic polypropylene. Isotactic polypropylene has historically been produced with heterogeneous catalysts that may be described as a catalyst on a solid support (e.g., titanium tetrachloride and aluminum alkyls on magnesium dichloride). This process typically uses hydrogen to control the molecular weight and electron-donor compounds to control the isotacticity. See also EP 0622380, U.S. Patent No. 4,297,465, U.S. Patent No. 5,385,993 and U.S. Patent No. 6,239,236.

[0008] Given the extensive research activities with respect to metallocene catalysts, there is continued interest in the next generation of non-cyclopentadienyl ligands for olefin polymerization catalysts providing attractive alternatives. See, e.g., "The Search for New-Generation Olefin Polymerization Catalysts: Life beyond Metallocenes", Gibson, et al., *Angew. Chem. Int. Ed.*, 1999, vol. 38, pp. 428-447; *Organometallics* 1999, 18, pp. 3649-3670. Recently, such systems have been discovered, see, e.g., U.S. 6,103,657 and U.S. 5,637,660. For isotactic polypropylene, bis-amide catalysts have been disclosed in U.S. Patent 5,318,935 and amidinate catalysts have been disclosed in WO 99/05186. See also U.S. Patent 6,214,939.

[0009] There remains a need for the discovery and optimization of non-cyclopentadienyl based catalysts for olefin polymerization, and in particular for certain polymers, such as isotactic polypropylene and ethylene-alpha-olefin copolymers. For a solution polymerization methodology, this need may be acute in view of the lack of versatile catalysts for the preparation of isotactic polypropylene at commercially acceptable temperatures. Indeed, new polymer properties are disclosed herein for isotactic polypropylene, ethylene-styrene copolymers and ethylene-isobutylene copolymers.

## SUMMARY OF THE INVENTION

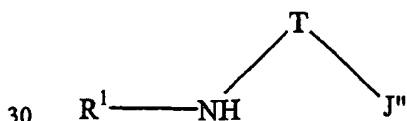
[0010] This invention discloses surprising enhanced catalytic performances for olefin polymerization when certain combinations of ligands and hafnium metal precursors are employed. This invention also discloses surprising enhanced catalytic performances for olefin polymerization when certain metal complexes are employed in a catalyst, including 2,1 metal complexes and 3,2 metal complexes. In addition, some of the ligands employed herein are themselves novel.

[0011] In some embodiments, this invention discloses both the preferred use of a hafnium metal center and certain pyridyl-amine ligands. Such combinations lead to new ligand-metal complexes, catalyst compositions and processes for the polymerization of olefins, diolefins, or other polymerizable monomers. In particular, copolymers of ethylene and another monomer may be prepared with controlled incorporation of the other monomer (e.g., 1-octene, isobutylene, or styrene) into the polymer backbone. In some embodiments, this control is adjusted so that the olefin incorporation is considered to be high with respect to polymers currently known or commercially available. Also in particular, propylene may be polymerized into very high molecular weight isotactic polypropylene. Thus, polymers having novel, improved or desired properties may be prepared using the catalysts and processes of this invention.

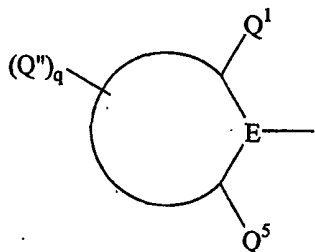
[0012] More specifically, in some embodiments, the use of a hafnium metal has been found to be preferred as compared to a zirconium metal for pyridyl-amine ligand catalysts. A broad range of ancillary ligand substituents may accommodate the enhanced catalytic performance. The catalysts in some embodiments are compositions comprising the ligand and metal precursor, and optionally may additionally include an activator, combination of activators or activator package.

[0013] The invention disclosed herein additionally includes catalysts comprising ancillary ligand-hafnium complexes, ancillary ligand-zirconium complexes and optionally activators, which catalyze polymerization and copolymerization reactions, particularly with monomers that are olefins, diolefins or other unsaturated compounds. Zirconium complexes, hafnium complexes, compositions or compounds using the disclosed ligands are within the scope of this invention. The metal-ligand complexes may be in a neutral or charged state. The ligand to metal ratio may also vary, the exact ratio being dependent on the nature of the ligand and metal-ligand complex. The metal-ligand complex or complexes may take different forms, for example, they may be monomeric, dimeric or higher orders thereof.

[0014] For example, suitable ligands useful in this invention may be characterized by the following general formula:



wherein  $R^1$  is a ring having from 4-8 atoms in the ring generally selected from the group consisting of substituted cycloalkyl, substituted heterocycloalkyl, substituted aryl and substituted heteroaryl, such that  $R^1$  may be characterized by the general formula:



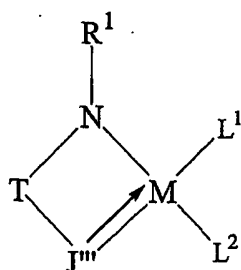
- 5 where  $Q^1$  and  $Q^5$  are substituents on the ring ortho to atom E, with E being selected from the group consisting of carbon and nitrogen and with at least one of  $Q^1$  or  $Q^5$  being bulky (defined as having at least 2 atoms).  $Q''_q$  represents additional possible substituents on the ring, with q being 1, 2, 3, 4 or 5 and  $Q''$  being selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, halide, nitro, and combinations thereof. T is a bridging group selected from the group consisting of  $-CR^2R^3-$  and  $-SiR^2R^3-$  with  $R^2$  and  $R^3$  being independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, halide, nitro, and combinations thereof. J' is generally selected from the group consisting of heteroaryl and substituted heteroaryl, with particular embodiments for particular reactions being described herein.
- 10 [0015] Also for example, in some embodiments, the ligands of the invention may be combined with a metal precursor compound that may be characterized by the general formula  $Hf(L)_n$  where L is independently selected from the group consisting of halide (F, Cl, Br, I), alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, hydroxy, boryl, silyl, amino, amine, hydrido, allyl, diene, seleno, phosphino, phosphine, carboxylates, thio, 1,3-dionates, oxalates, carbonates, nitrates, sulphates, ethers, thioethers and combinations thereof; and optionally two L groups may be linked together in a ring structure. n is 1, 2, 3, 4, 5, or 6.

[0016] In another aspect of the invention, a polymerization process is disclosed for monomers. The polymerization process involves subjecting one or more monomers to the catalyst compositions or complexes of this invention under polymerization conditions. The polymerization process can be continuous, batch or semi-batch and can be homogeneous, supported homogeneous or heterogeneous. Another aspect of this invention relates to arrays of ligands, metal precursors and/or metal-ligand complexes. These arrays are useful for the high speed or combinatorial materials science discovery or optimization of the catalyst compositions or complexes disclosed herein.

[0017] These catalysts comprising ancillary ligand-metal complexes or compositions comprising metal precursors and ligands and, optionally, activators are particularly effective at polymerizing  $\alpha$ -olefins (such as propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, and styrene), copolymerizing ethylene with  $\alpha$ -olefins (such as propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, and styrene), and copolymerizing ethylene with 1,1-disubstituted olefins (such as isobutylene). These compositions might also polymerize monomers that have polar functionalities in homopolymerizations or copolymerizations. Also, diolefins in combination with ethylene and/or  $\alpha$ -olefins or 1,1-disubstituted olefins may be copolymerized. The new catalyst compositions can be prepared by combining a hafnium precursor with a suitable ligand and, optionally, an activator or combination of activators. This invention discloses a novel class of catalysts and improved method for preparing isotactic polypropylene. The catalyst is useful for polymerizing a wide variety of polymerizable monomers.

[0018] In particular, a method of producing isotactic polypropylene in a solution process is disclosed and is surprisingly tunable. In one aspect, the temperature of the solution polymerization process can be increased, which generally decreases the molecular weight, but surprisingly, while maintaining a relatively high isotacticity of the polypropylene and while maintaining a relatively high melting point for the polypropylene. In another aspect, the temperature of the solution process can be increased without the molecular weight of the polypropylene dropping so low to levels that are unacceptable for certain commercial applications.

[0019] In certain aspects, it has been discovered that certain ligands complex to the metal resulting in novel complexes. In one aspect, the 3,2 metal-ligand complexes of this invention may be generally characterized by the following formula:



where M is zirconium or hafnium;

R<sup>1</sup> and T are defined above;

J<sup>'''</sup> being selected from the group of substituted heteroaryls with 2 atoms bonded to the metal M, at least one of those atoms being a heteroatom, and with one atom of J<sup>'''</sup> is bonded to M via a dative bond, the other through a covalent bond; and L<sup>1</sup> and L<sup>2</sup> are independently selected from the group consisting of halide, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, hydroxy, boryl, silyl, amino, amine, hydrido, allyl, diene, seleno, phosphino, phosphine, carboxylates, thio, 1,3-dionates, oxalates, carbonates, nitrates, sulphates, ethers, thioethers and combinations thereof; and optionally the L groups may be linked together in a ring structure.

[0020] In another aspect, a solution process to prepare isotactic polypropylene is provided comprising adding a catalyst and propylene monomer to a reactor and subjecting the contents to polymerization conditions, where the temperature of the solution process is at least 110°C and polypropylene is produced that has a weight average molecular weight of at least 100,000, without a drop off in tacticity value (*i.e.*, crystallinity index).

[0021] Thus, it is a feature of this invention to use hafnium-ligand complexes as polymerization catalysts with enhanced performance.

[0022] It is an object of this invention to polymerize olefins and unsaturated monomers with hafnium-ligand complexes. It is also an object of this invention to polymerize olefins and unsaturated monomers with compositions including substituted pyridyl amine ligands and hafnium metal precursors.

[0023] It is still a further object of this invention to polymerize olefins and unsaturated monomers with the hafnium-ligand complexes that additionally comprise an activator or combination of activators.



[0024] It is also an object of this invention to use non-metallocene group 4 complexes as polymerization catalysts for the production of isotactic polypropylene.

[0025] It is a further object of this invention to polymerize olefins and unsaturated monomers with a catalyst comprised of metal complexes comprising 3,2 ligands.

- 5 [0026] Further objects and aspects of this invention will be evident to those of skill in the art upon review of this specification.

### BRIEF DESCRIPTION OF THE DRAWINGS

- 10 [0027] Figure 1 depicts Table 1, which lists compounds that may be useful for synthesizing the ligands in this invention.

[0028] Figure 2 depicts Table 2, which lists other compounds that may be useful for synthesizing the ligands in this invention.

- [0029] Figure 3 depicts Table 3, which shows the ligands and results from examples,  
15 below, using the Hf metal precursor.

[0030] Figure 4 depicts Table 4, which shows the ligands and results from comparative examples, below, using the Zr metal precursor.

### DETAILED DESCRIPTION OF THE INVENTION

20

[0031] The inventions disclosed herein include metal complexes and compositions, which are useful as catalysts for polymerization reactions.

- [0032] As used herein, the phrase "characterized by the formula" is not intended to be limiting and is used in the same way that "comprising" is commonly used. The term  
25 "independently selected" is used herein to indicate that the R groups, e.g., R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, and R<sup>5</sup> can be identical or different (e.g. R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, and R<sup>5</sup> may all be substituted alkyls or R<sup>1</sup> and R<sup>2</sup> may be a substituted alkyl and R<sup>3</sup> may be an aryl, etc.). Use of the singular includes use of the plural and vice versa (e.g., a hexane solvent, includes hexanes). A named R group will generally have the structure that is recognized in the art  
30 as corresponding to R groups having that name. The terms "compound" and "complex" are generally used interchangeably in this specification, but those of skill in the art may recognize certain compounds as complexes and vice versa. For the purposes of illustration, representative certain groups are defined herein. These definitions are

intended to supplement and illustrate, not preclude, the definitions known to those of skill in the art.

5 [0033] "Hydrocarbyl" refers to univalent hydrocarbyl radicals containing 1 to about 30 carbon atoms, preferably 1 to about 24 carbon atoms, most preferably 1 to about 12 carbon atoms, including branched or unbranched, saturated or unsaturated species, such as alkyl groups, alkenyl groups, aryl groups, and the like. "Substituted hydrocarbyl" refers to hydrocarbyl substituted with one or more substituent groups, and the terms "heteroatom-containing hydrocarbyl" and "heterohydrocarbyl" refer to hydrocarbyl in which at least one carbon atom is replaced with a heteroatom.

10 [0034] The term "alkyl" is used herein to refer to a branched or unbranched, saturated or unsaturated acyclic hydrocarbon radical. Suitable alkyl radicals include, for example, methyl, ethyl, n-propyl, i-propyl, 2-propenyl (or allyl), vinyl, n-butyl, t-butyl, i-butyl (or 2-methylpropyl), etc. In particular embodiments, alkyls have between 1 and 200 carbon atoms, between 1 and 50 carbon atoms or between 1 and 20 carbon atoms.

15 [0035] "Substituted alkyl" refers to an alkyl as just described in which one or more hydrogen atom bound to any carbon of the alkyl is replaced by another group such as a halogen, aryl, substituted aryl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, halogen, alkylhalos (e.g., CF<sub>3</sub>), hydroxy, amino, phosphido, alkoxy, amino, thio, nitro, and combinations thereof. Suitable substituted alkyls include, 20 for example, benzyl, trifluoromethyl and the like.

[0036] The term "heteroalkyl" refers to an alkyl as described above in which one or more hydrogen atoms to any carbon of the alkyl is replaced by a heteroatom selected from the group consisting of N, O, P, B, S, Si, Sb, Al, Sn, As, Se and Ge. This same list of heteroatoms is useful throughout this specification. The bond between the carbon 25 atom and the heteroatom may be saturated or unsaturated. Thus, an alkyl substituted with a heterocycloalkyl, substituted heterocycloalkyl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, boryl, phosphino, amino, silyl, thio, or seleno is within the scope of the term heteroalkyl. Suitable heteroalkyls include cyano, benzoyl, 2-pyridyl, 2-furyl and the like.

30 [0037] The term "cycloalkyl" is used herein to refer to a saturated or unsaturated cyclic non-aromatic hydrocarbon radical having a single ring or multiple condensed rings. Suitable cycloalkyl radicals include, for example, cyclopentyl, cyclohexyl, cyclooctenyl, bicyclooctyl, etc. In particular embodiments, cycloalkyls have between 3 and 200

carbon atoms, between 3 and 50 carbon atoms or between 3 and 20 carbon atoms.

[0038] "Substituted cycloalkyl" refers to cycloalkyl as just described including in which one or more hydrogen atom to any carbon of the cycloalkyl is replaced by another group such as a halogen, alkyl, substituted alkyl, aryl, substituted aryl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, boryl, phosphino, amino, silyl, thio, seleno and combinations thereof. Suitable substituted cycloalkyl radicals include, for example, 4-dimethylaminocyclohexyl, 4,5-dibromocyclohept-4-enyl, and the like.

[0039] The term "heterocycloalkyl" is used herein to refer to a cycloalkyl radical as described, but in which one or more or all carbon atoms of the saturated or unsaturated cyclic radical are replaced by a heteroatom such as nitrogen, phosphorous, oxygen, sulfur, silicon, germanium, selenium, or boron. Suitable heterocycloalkyls include, for example, piperazinyl, morpholinyl, tetrahydropyranyl, tetrahydrofuran, piperidinyl, pyrrolidinyl, oxazolinyl and the like.

[0040] "Substituted heterocycloalkyl" refers to heterocycloalkyl as just described including in which one or more hydrogen atom to any atom of the heterocycloalkyl is replaced by another group such as a halogen, alkyl, substituted alkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, boryl, phosphino, amino, silyl, thio, seleno and combinations thereof. Suitable substituted heterocycloalkyl radicals include, for example, N-methylpiperazinyl, 3-dimethylaminomorpholinyl and the like.

[0041] The term "aryl" is used herein to refer to an aromatic substituent, which may be a single aromatic ring or multiple aromatic rings that are fused together, linked covalently, or linked to a common group such as a methylene or ethylene moiety. The aromatic ring(s) may include phenyl, naphthyl, anthracenyl, and biphenyl, among others. In particular embodiments, aryls have between 1 and 200 carbon atoms, between 1 and 50 carbon atoms or between 1 and 20 carbon atoms. In some embodiments herein, multi-ring moieties are substituents and in such an embodiment the multi-ring moiety can be attached at an appropriate atom. For example, "naphthal" can be 1-naphthyl or 2-naphthyl; "anthracenyl" can be 1-anthracenyl, 2-anthracenyl or 9-anthracenyl; and "phenanthrenyl" can be 1-phenanthrenyl, 2-phenanthrenyl, 3-phenanthrenyl, 4-phenanthrenyl or 9-phenanthrenyl.

[0042] "Substituted aryl" refers to aryl as just described in which one or more hydrogen atom bound to any carbon is replaced by one or more functional groups such as alkyl,

substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, halogen, alkylhalos (e.g.,  $\text{CF}_3$ ), hydroxy, amino, phosphido, alkoxy, amino, thio, nitro, and both saturated and unsaturated cyclic hydrocarbons which are fused to the aromatic ring(s), linked covalently or linked to a common group such as a methylene or ethylene moiety. The common linking group may also be a carbonyl as in benzophenone or oxygen as in diphenylether or nitrogen in diphenylamine.

[0043] The term "heteroaryl" as used herein refers to aromatic or unsaturated rings in which one or more carbon atoms of the aromatic ring(s) are replaced by a heteroatom(s) such as nitrogen, oxygen, boron, selenium, phosphorus, silicon or sulfur. Heteroaryl refers to structures that may be a single aromatic ring, multiple aromatic ring(s), or one or more aromatic rings coupled to one or more non-aromatic ring(s). In structures having multiple rings, the rings can be fused together, linked covalently, or linked to a common group such as a methylene or ethylene moiety. The common linking group may also be a carbonyl as in phenyl pyridyl ketone. As used herein, rings such as thiophene, pyridine, isoxazole, pyrazole, pyrrole, furan, etc. or benzo-fused analogues of these rings are defined by the term "heteroaryl."

[0044] "Substituted heteroaryl" refers to heteroaryl as just described including in which one or more hydrogen atoms bound to any atom of the heteroaryl moiety is replaced by another group such as a halogen, alkyl, substituted alkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, boryl, phosphino, amino, silyl, thio, selenium and combinations thereof. Suitable substituted heteroaryl radicals include, for example, 4-N,N-dimethylaminopyridine.

[0045] The term "alkoxy" is used herein to refer to the  $-\text{OZ}^1$  radical, where  $\text{Z}^1$  is selected from the group consisting of alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, silyl groups and combinations thereof as described herein. Suitable alkoxy radicals include, for example, methoxy, ethoxy, benzyloxy, t-butoxy, etc. A related term is "aryloxy" where  $\text{Z}^1$  is selected from the group consisting of aryl, substituted aryl, heteroaryl, substituted heteroaryl, and combinations thereof. Examples of suitable aryloxy radicals include phenoxy, substituted phenoxy, 2-pyridinoxy, 8-quinolinoxy and the like.

[0046] As used herein the term "silyl" refers to the  $-\text{SiZ}^1\text{Z}^2\text{Z}^3$  radical, where each of  $\text{Z}^1$ ,  $\text{Z}^2$ , and  $\text{Z}^3$  is independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, heterocycloalkyl, heterocyclic, aryl, substituted aryl,

heteroaryl, substituted heteroaryl, alkoxy, aryloxy, amino, silyl and combinations thereof.

[0047] As used herein the term "boryl" refers to the  $-BZ^1Z^2$  group, where each of  $Z^1$  and  $Z^2$  is independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, heterocycloalkyl, heterocyclic, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, amino, silyl and combinations thereof.

[0048] As used herein, the term "phosphino" refers to the group  $-PZ^1Z^2$ , where each of  $Z^1$  and  $Z^2$  is independently selected from the group consisting of hydrogen, substituted or unsubstituted alkyl, cycloalkyl, heterocycloalkyl, heterocyclic, aryl, substituted aryl, heteroaryl, silyl, alkoxy, aryloxy, amino and combinations thereof.

[0049] As used herein, the term "phosphine" refers to the group  $:PZ^1Z^2Z^3$ , where each of  $Z^1$ ,  $Z^3$  and  $Z^2$  is independently selected from the group consisting of hydrogen, substituted or unsubstituted alkyl, cycloalkyl, heterocycloalkyl, heterocyclic, aryl, substituted aryl, heteroaryl, silyl, alkoxy, aryloxy, amino and combinations thereof.

[0050] The term "amino" is used herein to refer to the group  $-NZ^1Z^2$ , where each of  $Z^1$  and  $Z^2$  is independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl and combinations thereof.

[0051] The term "amine" is used herein to refer to the group  $:NZ^1Z^2Z^3$ , where each of  $Z^1$ ,  $Z^2$  and  $Z^3$  is independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl (including pyridines), substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl and combinations thereof.

[0052] The term "thio" is used herein to refer to the group  $-SZ^1$ , where  $Z^1$  is selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl and combinations thereof.

[0053] The term "seleno" is used herein to refer to the group  $-SeZ^1$ , where  $Z^1$  is selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl and combinations thereof.

[0054] The term "saturated" refers to lack of double and triple bonds between atoms of a

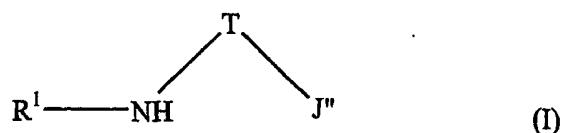
radical group such as ethyl, cyclohexyl, pyrrolidinyl, and the like.

[0055] The term "unsaturated" refers to the presence one or more double and triple bonds between atoms of a radical group such as vinyl, acetylide, oxazolinyl, cyclohexenyl, acetyl and the like.

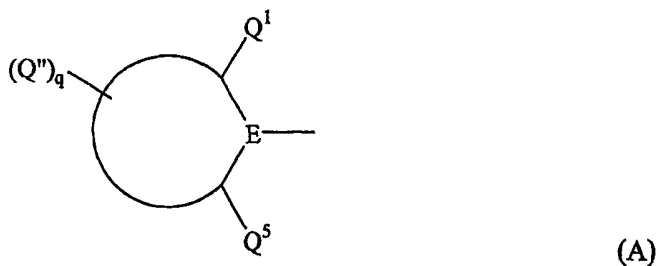
- 5 [0056] Other abbreviations used herein include: "Pr" to refer to isopropyl; "Bu" to refer to tertbutyl; "Me" to refer to methyl; and "Et" to refer to ethyl.

### Ligands

- [0057] Suitable ligands useful in this invention can be characterized broadly as  
 10 monoanionic ligands having an amine and a heteroaryl or substituted heteroaryl group.  
 The ligand substituents for particular monomers are detailed near the end of this section.  
 The ligands of the invention may be characterized by the following general formula:



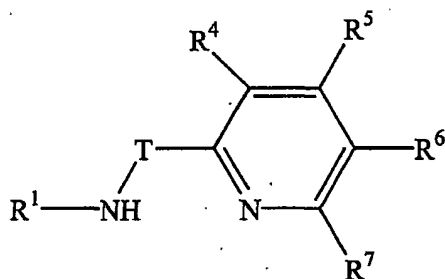
- wherein  $\text{R}^1$  is generally selected from the group consisting of alkyl, substituted alkyl,  
 15 cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl,  
 substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl and  
 combinations thereof. In many embodiments,  $\text{R}^1$  is a ring having from 4-8 atoms in the  
 ring generally selected from the group consisting of substituted cycloalkyl, substituted  
 heterocycloalkyl, substituted aryl and substituted heteroaryl, with  $\text{R}^1$  being characterized  
 20 by the general formula:



- where  $\text{Q}^1$  and  $\text{Q}^5$  are substituents on the ring ortho to atom E, with E being selected from  
 the group consisting of carbon and nitrogen and with at least one of  $\text{Q}^1$  or  $\text{Q}^5$  being bulky  
 (defined as having at least 2 non-hydrogen atoms).  $\text{Q}^1$  and  $\text{Q}^5$  are independently selected  
 25 from the group consisting of alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl,  
 aryl, substituted aryl and silyl, but provided that  $\text{Q}^1$  and  $\text{Q}^5$  are not both methyl.  $\text{Q}''_q$   
 represents additional possible substituents on the ring, with q being 1, 2, 3, 4 or 5 and  $\text{Q}''$

being selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, halide, nitro, and combinations thereof. T is a bridging group selected group consisting of  $-CR^2R^3-$  and  $-SiR^2R^3-$  with  $R^2$  and  $R^3$  being independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, halide, nitro, and combinations thereof. J" is generally selected from the group consisting of heteroaryl and substituted heteroaryl, with particular embodiments for particular reactions being described herein.

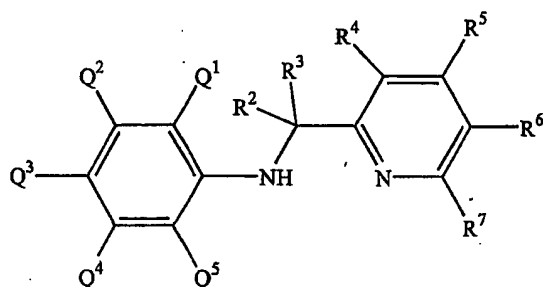
[0058] In a more specific embodiment, suitable ligands useful in this invention may be characterized by the following general formula:



(II)

wherein  $R^1$  and T are as defined above and each of  $R^4$ ,  $R^5$ ,  $R^6$  and  $R^7$  is independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, halide, nitro, and combinations thereof. Optionally, any combination of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  may be joined together in a ring structure.

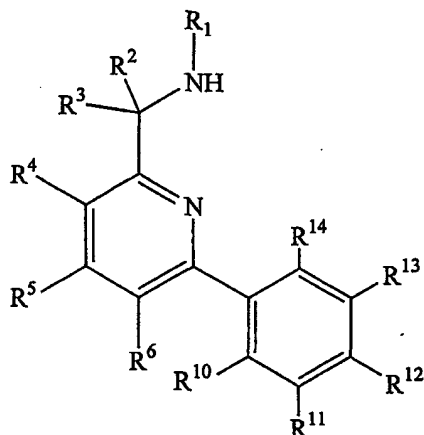
[0059] In certain more specific embodiments, the ligands in this invention may be characterized by the following general formula:



(III)

wherein  $Q^1$ ,  $Q^5$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$  and  $R^7$  are as defined above.  $Q^2$ ,  $Q^3$  and  $Q^4$  are independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, nitro, and combinations thereof.

[0060] In other more specific embodiments, the ligands of this invention and suitable herein may be characterized by the following general formula:



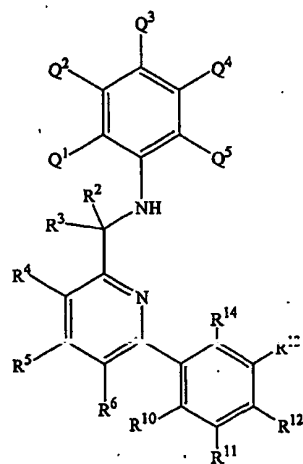
(IV)

wherein  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ , and  $R^6$  are as defined above. In this embodiment the  $R^7$  substituent has been replaced with an aryl or substituted aryl group, with  $R^{10}$ ,  $R^{11}$ ,  $R^{12}$  and  $R^{13}$  being independently selected from the group consisting of hydrogen, halide, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, nitro, and combinations thereof; optionally, two or more  $R^{10}$ ,  $R^{11}$ ,  $R^{12}$  and  $R^{13}$  groups may be joined to form a fused ring system having from 3-50 non-hydrogen atoms.  $R^{14}$  is selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl,



substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, halide, nitro, and combinations thereof.

[0061] In still more specific embodiments, the ligands in this invention may be characterized by the general formula:



(V)

wherein  $R^2$ - $R^6$ ,  $R^{10}$ - $R^{14}$  and  $Q^1$ - $Q^5$  are all as define above.

[0062] In certain embodiments,  $R^2$  is preferably hydrogen. Also preferably, each of  $R^4$  and  $R^5$  is hydrogen and  $R^6$  is either hydrogen or is joined to  $R^7$  to form a fused ring system. Also preferred is where  $R^3$  is selected from the group consisting of benzyl, phenyl, naphthyl, 2-biphenyl, t-butyl, 2-dimethylaminophenyl (2-(NMe<sub>2</sub>)-C<sub>6</sub>H<sub>4</sub>-), 2-methoxyphenyl (2-MeO-C<sub>6</sub>H<sub>4</sub>-), anthracenyl, mesityl, 2-pyridyl, 3,5-dimethylphenyl, o-tolyl and phenanthrenyl. Also preferred is where  $R^1$  is selected from the group consisting of mesityl, 4-isopropylphenyl (4-Pr<sup>i</sup>-C<sub>6</sub>H<sub>4</sub>-), naphthyl, 3,5-(CF<sub>3</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>-, 2-Me-naphthyl, 2,6-(Pr<sup>i</sup>)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>-, 2-biphenyl, 2-Me-4-MeO-C<sub>6</sub>H<sub>3</sub>-, 2-Bu<sup>t</sup>-C<sub>6</sub>H<sub>4</sub>-, 2,5-(Bu<sup>t</sup>)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>-, 2-Pr<sup>i</sup>-6-Me-C<sub>6</sub>H<sub>3</sub>-, 2-Bu<sup>t</sup>-6-Me-C<sub>6</sub>H<sub>3</sub>-, 2,6-Et<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>- or 2-sec-butyl-6-Et-C<sub>6</sub>H<sub>3</sub>-. Also preferred is where  $R^7$  is selected from the group consisting of hydrogen, phenyl, naphthyl, methyl, anthracenyl, phenanthrenyl, mesityl, 3,5-(CF<sub>3</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>-, 2-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-, 4-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-, 3,5-F<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>-, 4-F-C<sub>6</sub>H<sub>4</sub>-, 2,4-F<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>-, 4-(NMe<sub>2</sub>)-C<sub>6</sub>H<sub>4</sub>-, 3-MeO-C<sub>6</sub>H<sub>4</sub>-, 4-MeO-C<sub>6</sub>H<sub>4</sub>-, 3,5-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>-, o-tolyl, 2,6-F<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>- or where  $R^7$  is joined together with  $R^6$  to form a fused ring system, e.g., quinoline. In some preferred embodiment,  $R^4$ ,  $R^5$  and  $R^6$  are each independently selected from the group consisting of alkyl, aryl, halide, alkoxy, aryloxy, amino, and thio.

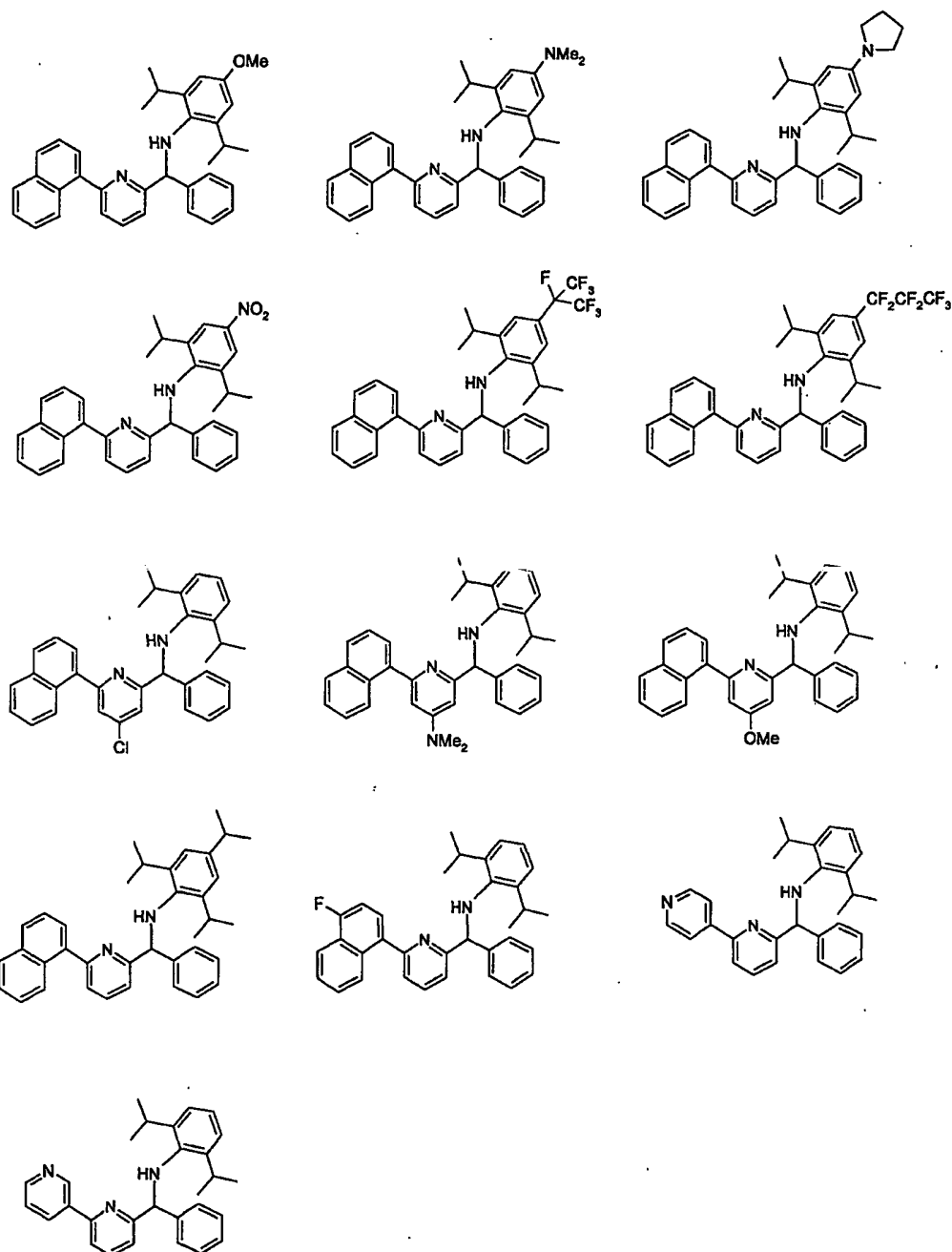
[0063] In some embodiments,  $Q^1$  and  $Q^5$  are, independently, selected from the group

consisting of  $-\text{CH}_2\text{R}^{15}$ ,  $-\text{CHR}^{16}\text{R}^{17}$  and methyl, provided that not both  $\text{Q}^1$  and  $\text{Q}^5$  are methyl. In these embodiments,  $\text{R}^{15}$  is selected from the group consisting of alkyl, substituted alkyl, aryl and substituted aryl.  $\text{R}^{16}$  and  $\text{R}^{17}$  are independently selected from the group consisting of alkyl, substituted alkyl, aryl and substituted aryl; and optionally  
5  $\text{R}^{16}$  and  $\text{R}^{17}$  are joined together in a ring structure having from 3-50 non-hydrogen atoms.

[0064] Also optionally, two or more  $\text{R}^4$ ,  $\text{R}^5$ ,  $\text{R}^6$ ,  $\text{R}^7$  groups may be joined to form a fused ring system having from 3-50 non-hydrogen atoms in addition to the pyridine ring, e.g. generating a quinoline group. In these embodiments,  $\text{R}^3$  is selected from the group consisting of aryl, substituted aryl, heteroaryl, substituted heteroaryl, primary and  
10 secondary alkyl groups, and  $-\text{PY}_2$  where Y is selected from the group consisting of aryl, substituted aryl, heteroaryl, and substituted heteroaryl.

[0065] Optionally within above formulas IV and V,  $\text{R}^6$  and  $\text{R}^{10}$  may be joined to form a ring system having from 5-50 non-hydrogen atoms. For example, if  $\text{R}^6$  and  $\text{R}^{10}$  together form a methylene, the ring will have 5 atoms in the backbone of the ring, which may or  
15 may not be substituted with other atoms. Also for example, if  $\text{R}^6$  and  $\text{R}^{10}$  together form an ethylene, the ring will have 6 atoms in the backbone of the ring, which may or may not be substituted with other atoms. Substituents from the ring can be selected from the group consisting of halide, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl,  
20 substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, nitro, and combinations thereof.

[0066] Specific examples of ligands within the scope of these formulas include:

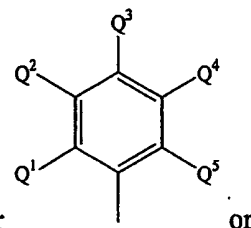


[0067] In certain embodiments, the ligands are novel compounds and those of skill in the art will be able to identify such compounds from the above. One example of the novel ligand compounds, includes those compounds generally characterized by formula (III),  
 5 above where  $R^2$  is selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, aryl, and substituted aryl; and  $R^3$  is a phosphino- characterized by the formula  $-PZ^1Z^2$ , where each of  $Z^1$  and  $Z^2$  is independently selected

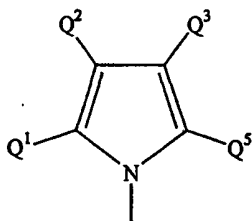
from the group consisting of hydrogen, substituted or unsubstituted alkyl, cycloalkyl, heterocycloalkyl, heterocyclic, aryl, substituted aryl, heteroaryl, silyl, alkoxy, aryloxy, amino and combinations thereof. Particularly preferred embodiments of these compounds include those where  $Z^1$  and  $Z^2$  are each independently selected from the group consisting of alkyl, substituted alkyl, cycloalkyl, heterocycloalkyl, aryl, and substituted aryl; and more specifically phenyl; where  $Q^1$ ,  $Q^3$ , and  $Q^5$  are each selected from the group consisting of alkyl and substituted alkyl and each of  $Q^2$  and  $Q^4$  is hydrogen; and where  $R^4$ ,  $R^5$ ,  $R^6$  and  $R^7$  are each hydrogen.

[0068] Certain embodiments of these ligands are preferred for the polymerization of certain monomers. In any of the above formulas I, II, III, IV or V, for the production of isotactic polypropylene it is an aspect of this invention that  $R^2$  cannot be the same group as  $R^3$ , leading to a chiral center on the carbon atom from which  $R^2$  and  $R^3$  stem. Thus, generally,  $R^3$  may be selected from the group consisting of hydrogen, halide, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, nitro, and combinations thereof, but it has also been learned that for isotactic polypropylene production  $R^3$  is aryl, substituted aryl, heteroaryl or substituted heteroaryl. In more specific embodiments for isotactic polypropylene production  $R^3$  is selected from the group consisting of benzyl, phenyl, naphthyl, 2-biphenyl, 2-dimethylaminophenyl, 2-methoxyphenyl, anthracenyl, mesityl, 2-pyridyl, 3,5-dimethylphenyl, o-tolyl, or phenanthrenyl. Also here,  $R^1$  is selected from the group consisting of 2,6-( $\text{Pr}^i$ )<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>-, 2- $\text{Pr}^i$ -6-Me-C<sub>6</sub>H<sub>3</sub>-, 2,6-Et<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>- or 2-sec-butyl-6-Et-C<sub>6</sub>H<sub>3</sub>-.

[0069] Also for isotactic polypropylene production it is preferred that within formula A, above, it is currently preferred that  $Q^1$  and  $Q^5$  are alkyl, substituted alkyl, heteroalkyl, substituted heteroalkyl, silyl, cycloalkyl, or substituted cycloalkyl, provided that  $Q^1$  and  $Q^5$  are not both methyl. Here also,  $Q^1$  and  $Q^5$  can be, independently, selected from the group consisting of  $-\text{CH}_2\text{R}^{15}$ ,  $-\text{CHR}^{16}\text{R}^{17}$  and methyl, provided that not both  $Q^1$  and  $Q^5$  are methyl. In a more specific embodiment for isotactic polypropylene production, it is currently preferred that  $Q^1$  and  $Q^5$  are both isopropyl; or both ethyl; or both sec-butyl; or  $Q^1$  is methyl and  $Q^5$  is isopropyl; or  $Q^1$  is ethyl and  $Q^5$  is sec-butyl. Even more



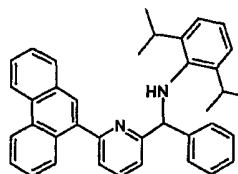
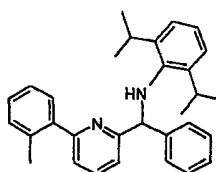
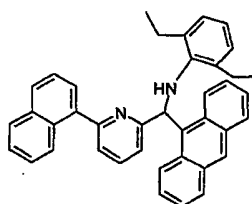
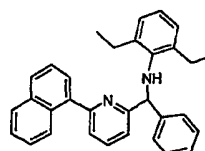
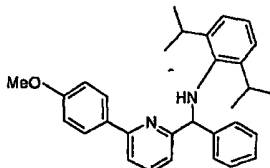
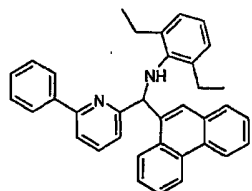
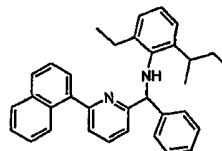
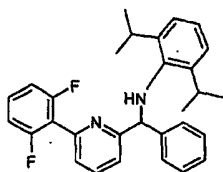
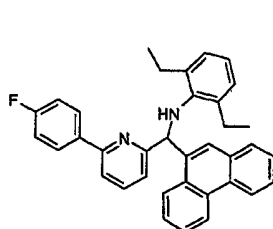
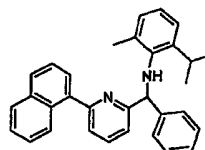
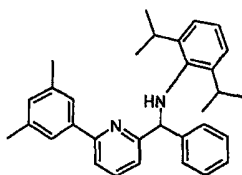
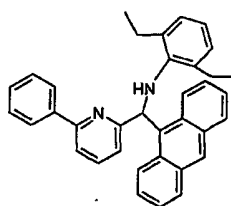
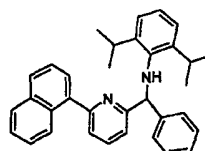
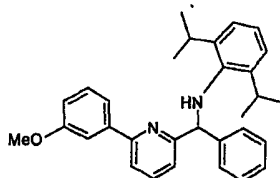
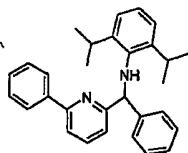
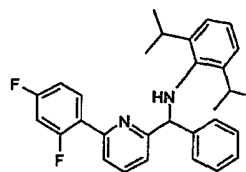
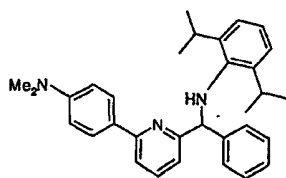
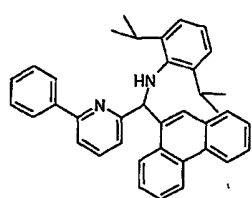
specifically, with these  $Q^1$  and  $Q^5$  preferences,  $R^1$  is either

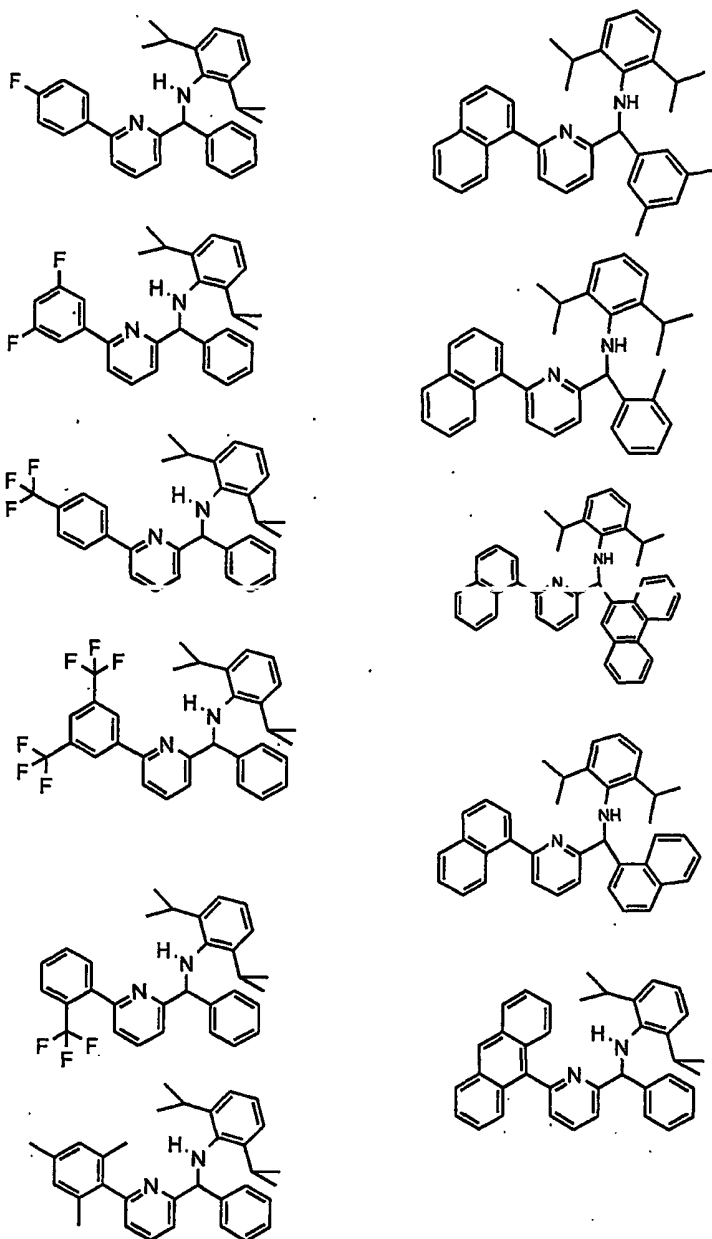


with the above definitions of the variables applying.

[0070] For isotactic polypropylene production it is preferred  $R^7$  is aryl, substituted aryl, heteroaryl or substituted heteroaryl, and more specifically  $R^7$  is phenyl, naphthyl, mesityl, anthracenyl or phenanthrenyl. Thus, most preferably, formulas IV and V above apply to isotactic polypropylene production, with it currently being preferred that  $R^{10}$ ,  $R^{11}$ ,  $R^{12}$ ,  $R^{13}$ , are each hydrogen; or one or more of  $R^{10}$ ,  $R^{11}$ ,  $R^{12}$ ,  $R^{13}$  are methyl, fluoro, trifluoromethyl, methoxy, or dimethylamino; or where  $R^{10}$  and  $R^{11}$  are joined to form a benzene ring and  $R^{12}$  and  $R^{13}$  are each hydrogen (thus forming a naphthyl group with the existing phenyl ring).

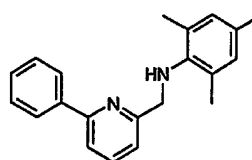
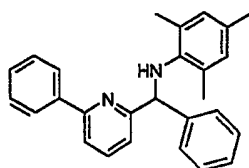
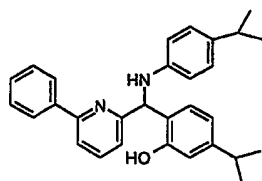
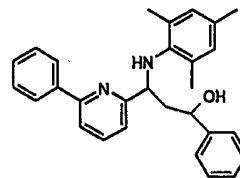
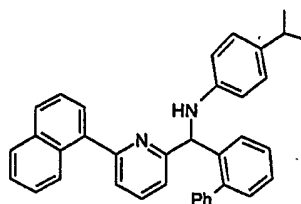
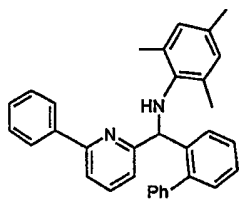
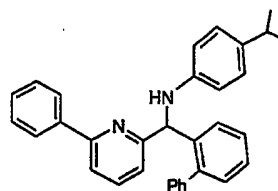
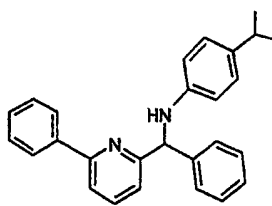
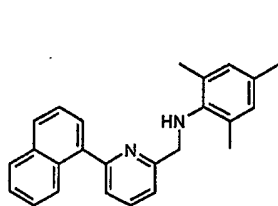
[0071] Specific ligands that are preferred for the production of crystalline polypropylene are:



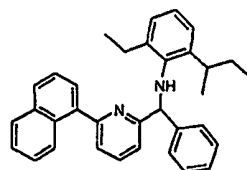
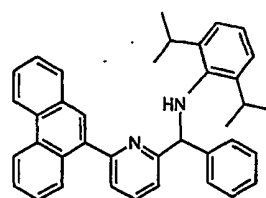
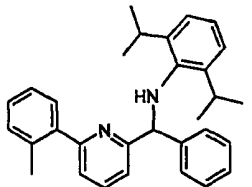
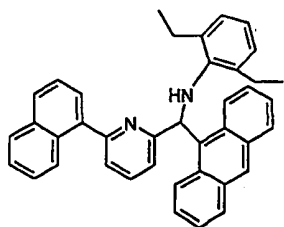
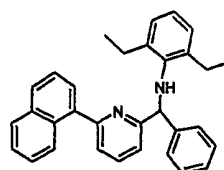
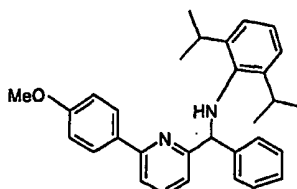
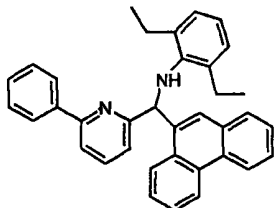
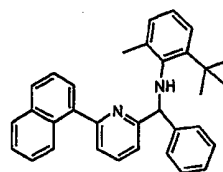
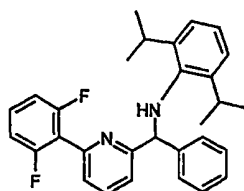
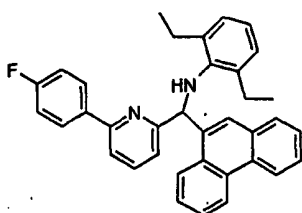
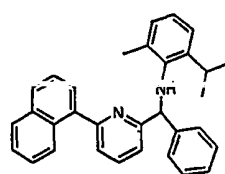
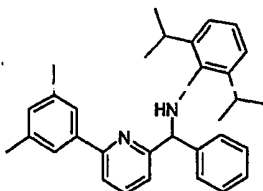
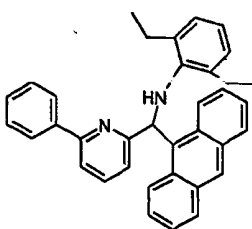
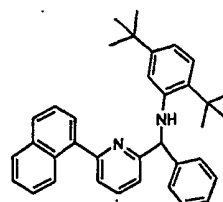
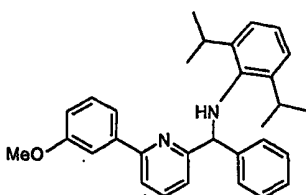
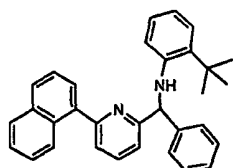
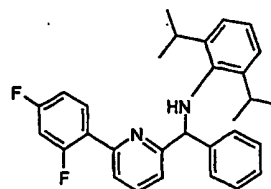
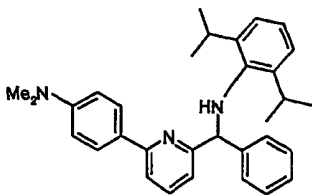
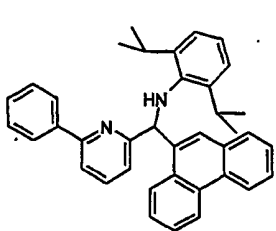


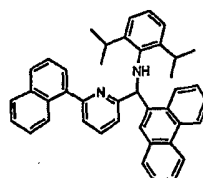
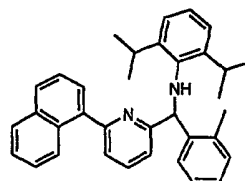
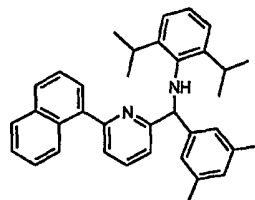
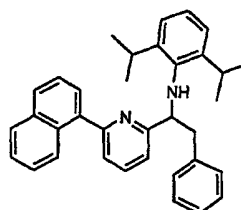
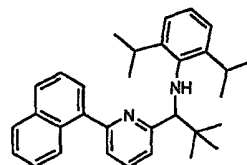
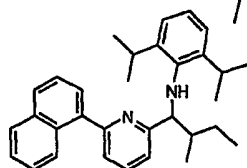
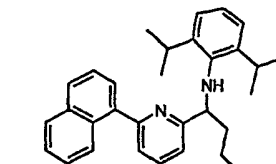
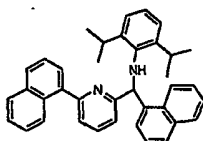
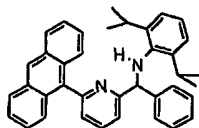
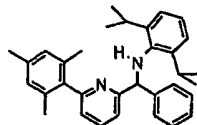
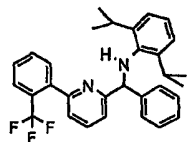
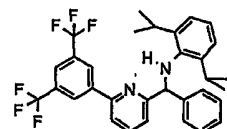
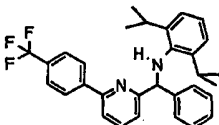
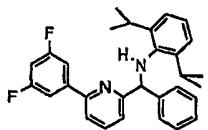
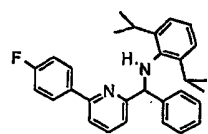
[0072] For the production of ethylene-styrene copolymers, there are different preferences depending on the type of polymer that is desired. In some embodiments, it is preferred that the ligands of either of formulas II, III, IV or V is used, particularly with R<sup>7</sup> selected from the group consisting of aryl, substituted aryl, heteroaryl, and substituted heteroaryl.

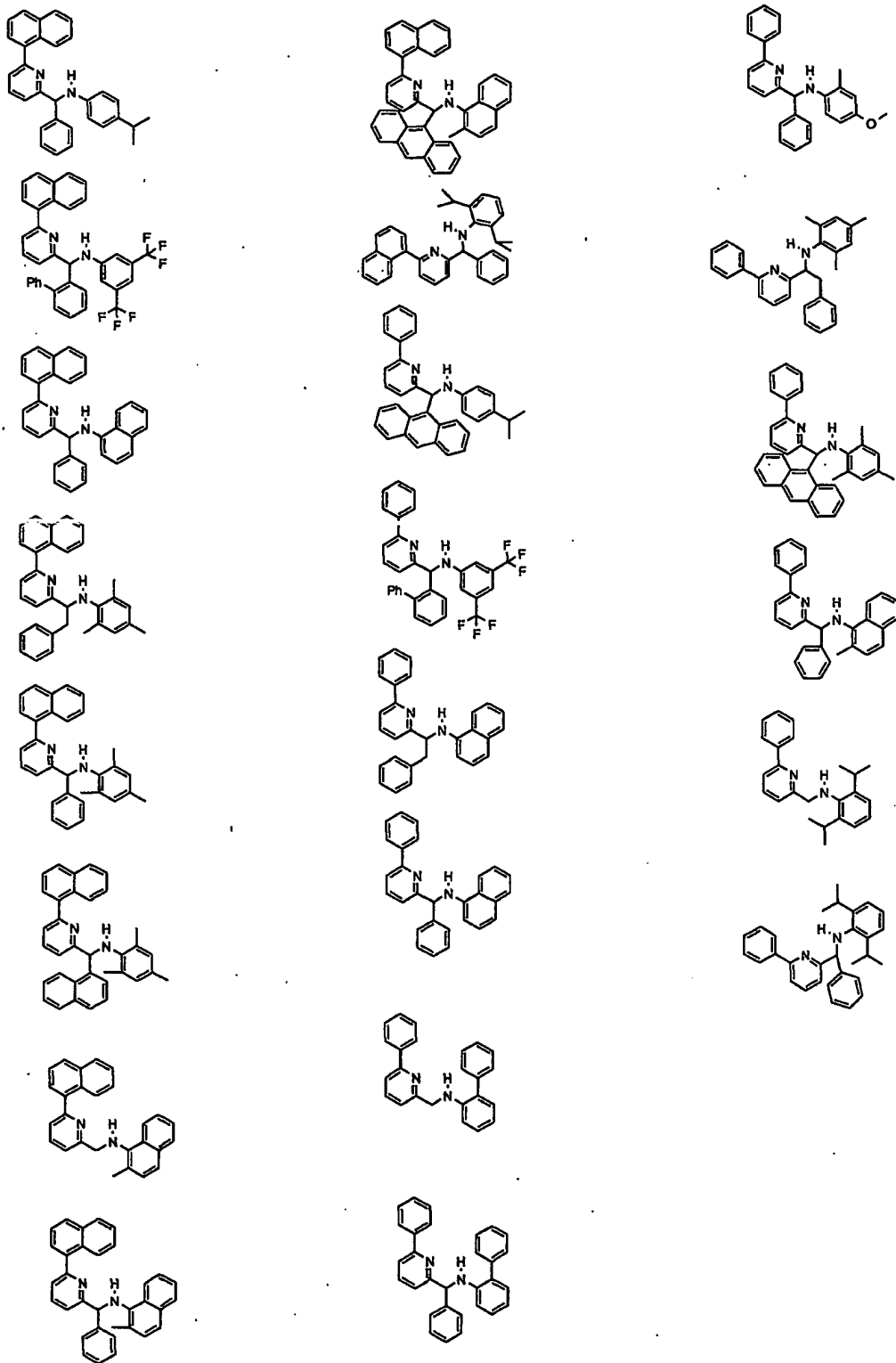
5 Specific ligands that are preferred for ethylene-styrene copolymer production are:





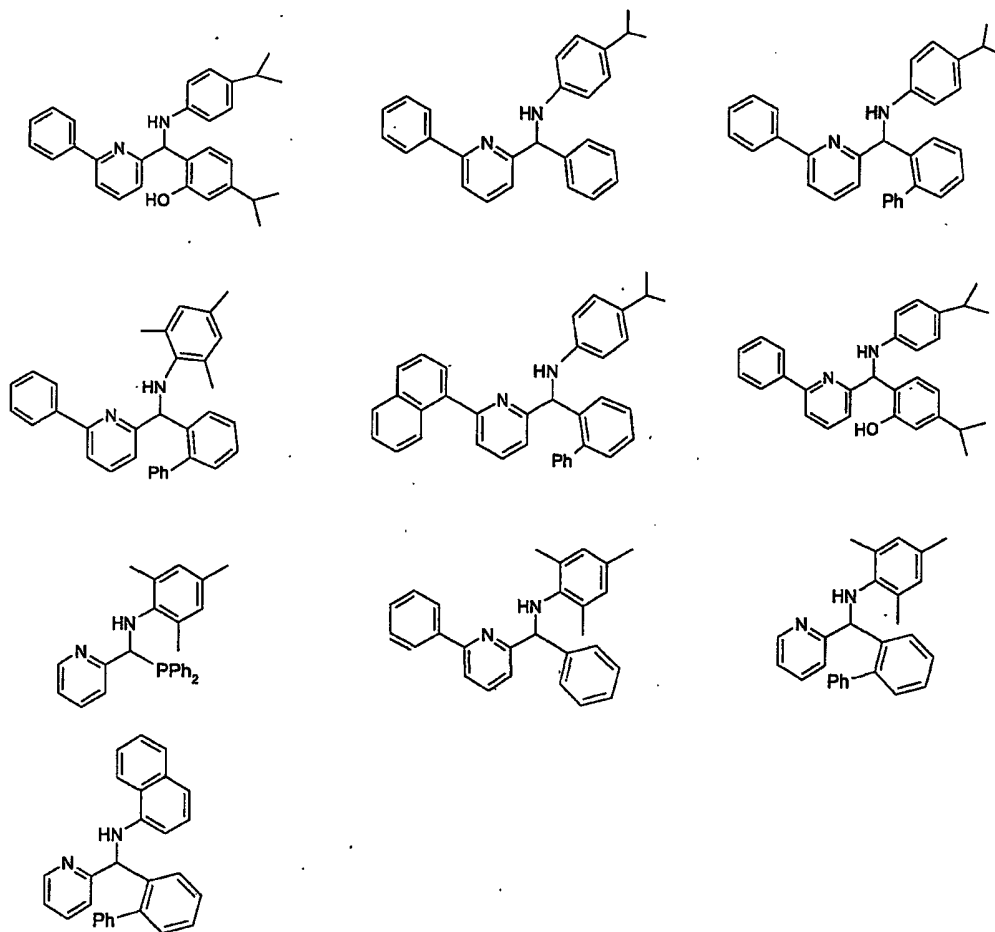


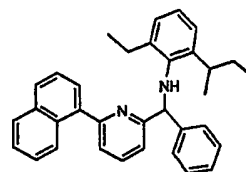
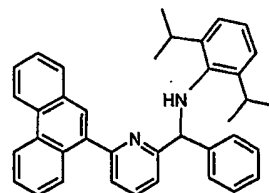
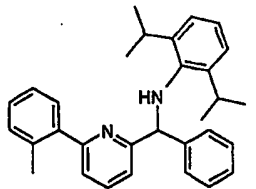
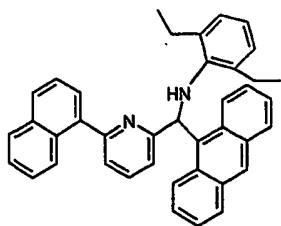
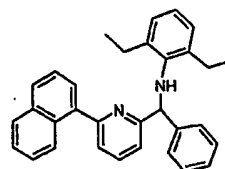
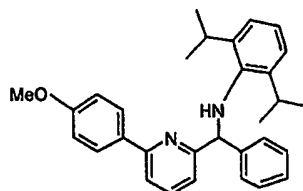
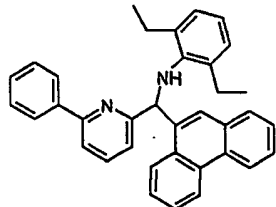
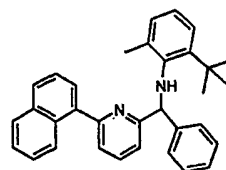
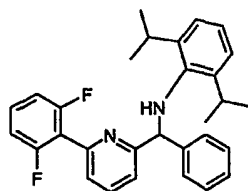
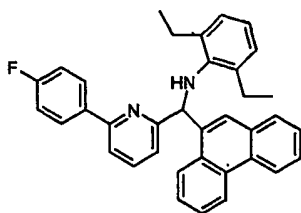
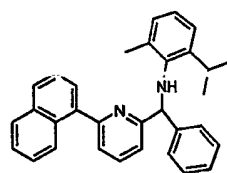
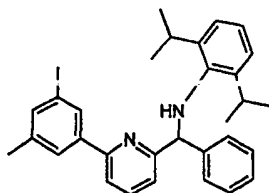
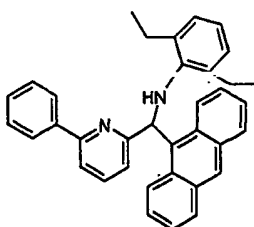
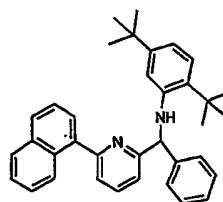
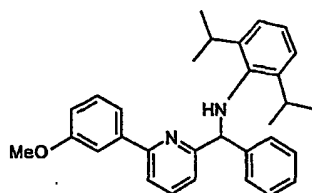
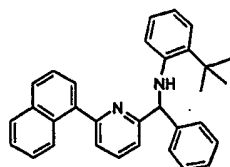
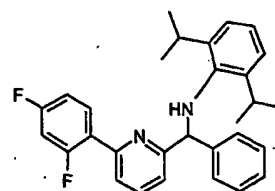
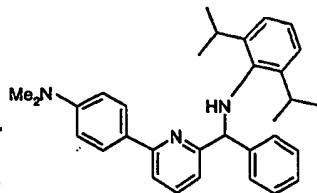
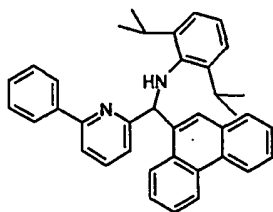


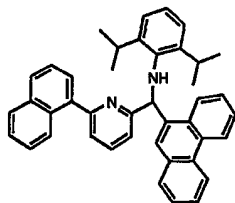
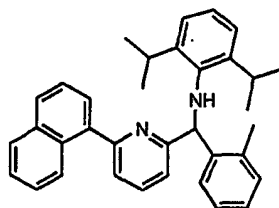
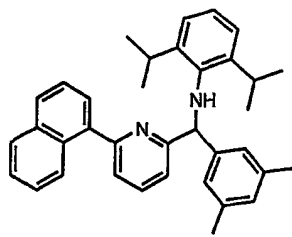
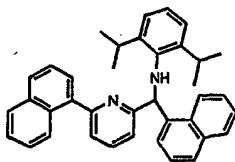
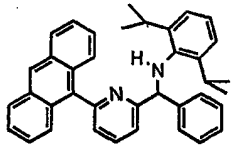
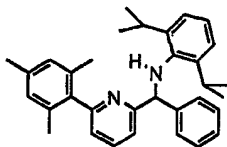
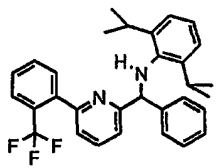
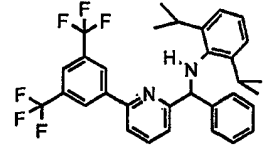
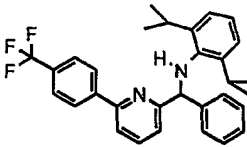
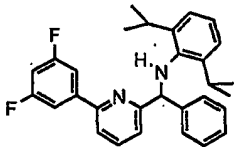
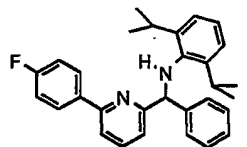


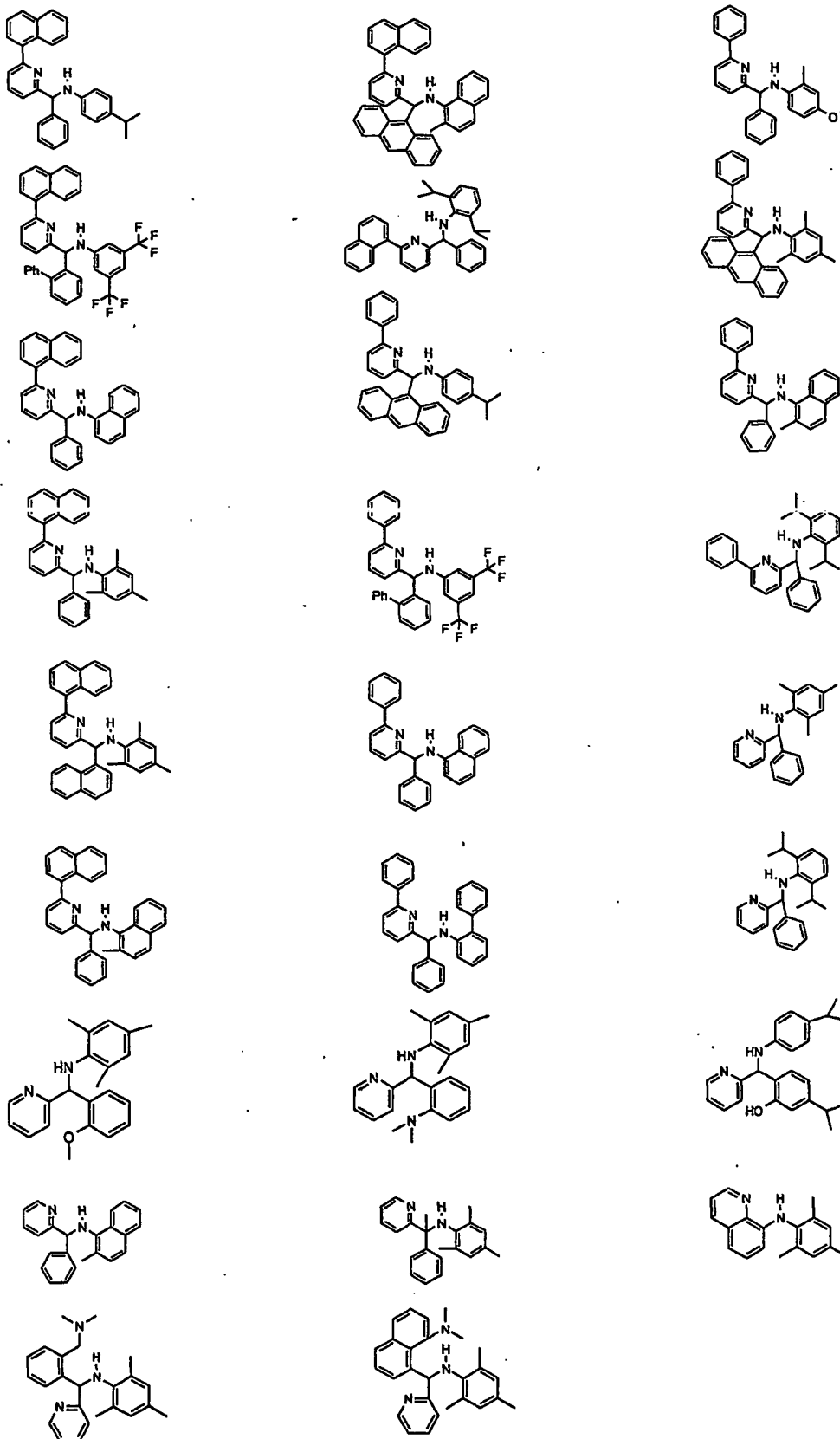
[0073] For the production of ethylene-1-octene copolymers, it is preferred that the ligands of either of formulas II, III, IV or V is used, with either or both of  $R^3$  and/or  $R^7$

being independently selected from the group consisting of aryl, substituted aryl, heteroaryl, and substituted heteroaryl. Specific ligands that are preferred for ethylene-1-octene copolymer production are:

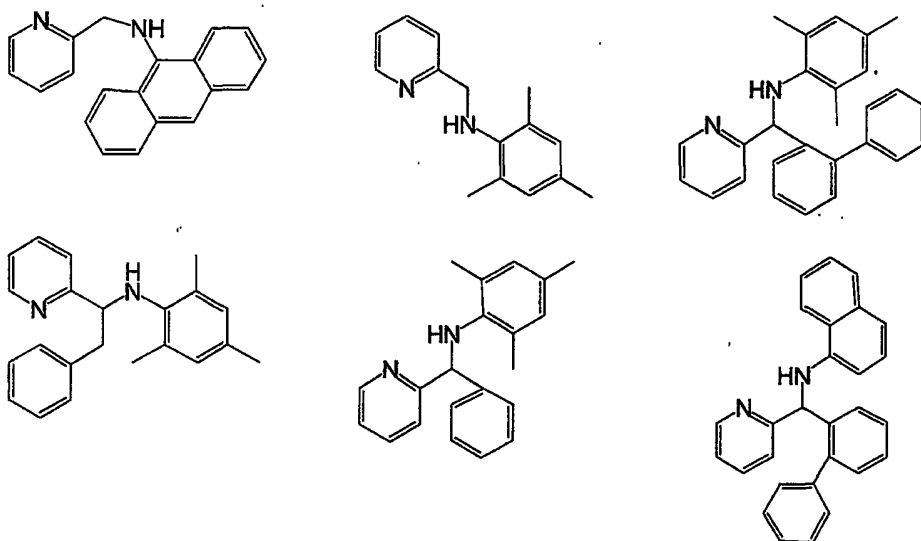






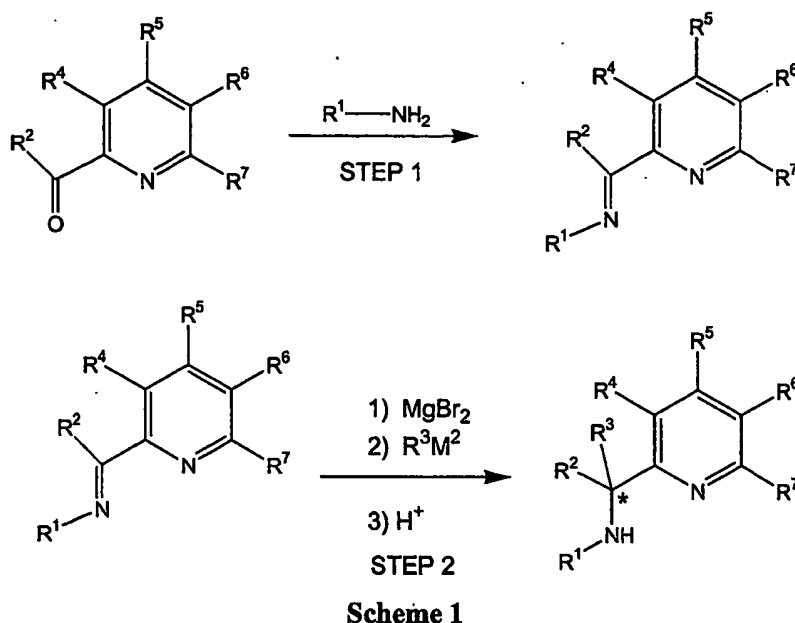


[0074] For the production of ethylene-isobutylene copolymers, it is currently preferred that  $R^2$  and  $R^3$  are either both hydrogen or  $R^2$  is hydrogen and  $R^3$  is aryl, substituted aryl or substituted alkyl. It is also important for ethylene-isobutylene copolymerization that  $R^7$  is hydrogen. Specific ligands useful in this invention for the production of ethylene-isobutylene copolymers include:

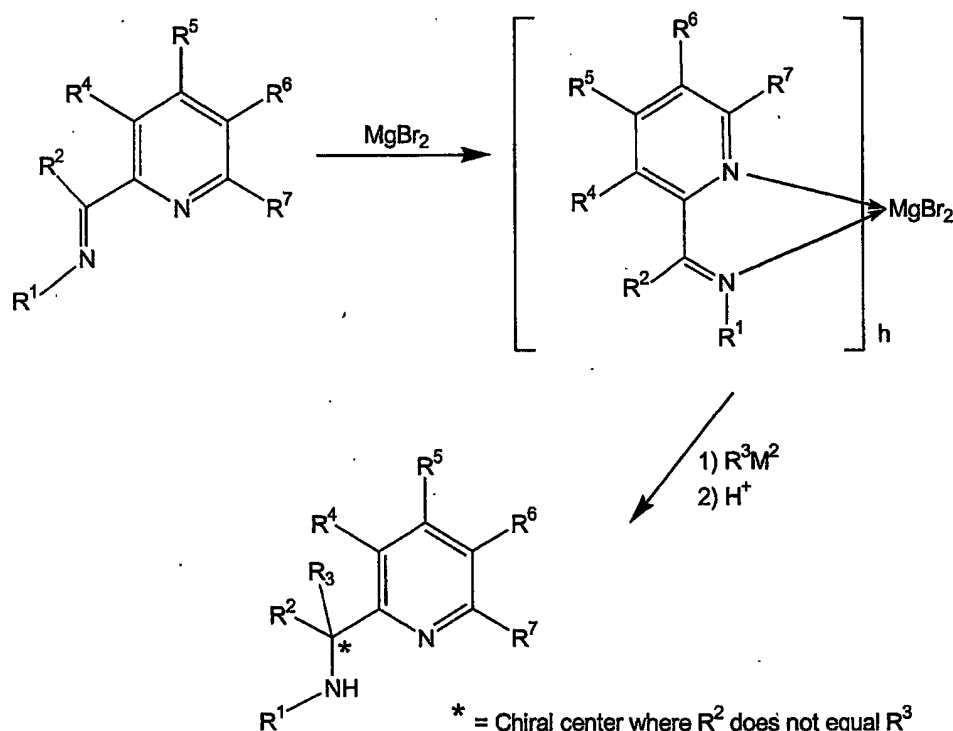


[0075] The ligands of the invention may be prepared using known procedures. See, for example, Advanced Organic Chemistry, March, Wiley, New York 1992 (4<sup>th</sup> Ed.). Specifically, the ligands of the invention may be prepared using the two step procedure outlined in Scheme 1.





- [0076] In Scheme 1, the \* represents a chiral center when  $R^2$  and  $R^3$  are not identical; also, the R groups have the same definitions as above. Generally,  $R^3M^2$  is a nucleophile such as an alkylating or arylating or hydrogenating reagent and  $M^2$  is a metal such as a main group metal, or a metalloid such as boron. The alkylating, arylating or hydrogenating reagent may be a Grignard, alkyl, aryl-lithium or borohydride reagent. Scheme 1, step 2 first employs the use of complexing reagent. Preferably, as in the case of Scheme 1, magnesium bromide is used as the complexing reagent. The role of the complexing reagent is to direct the nucleophile,  $R^3M^2$ , selectively to the imine carbon. Where the presence of functional groups impede this synthetic approach, alternative synthetic strategies may be employed. For instance, ligands where  $R^3$  = phosphino can be prepared in accordance with the teachings of U.S. 6,034,240 and U.S. 6,043,363. In addition, tetra-alkylhafnium compounds or tetra-substituted alkylhafnium compounds or tetra-arylhafnium compounds or tetra-substituted arylhafnium compounds may be employed in step 2, in accordance with the teachings of U.S. 6,103,657, which is incorporated herein by reference. Scheme 2 further describes a synthesis process:



Scheme 2

[0077] In scheme 2,  $h = 1$  or  $2$  and the bromine ions may or may not be bound to the magnesium. The effect of the complexation is to guide the subsequent nucleophilic attack by  $R^3M^2$  to the imine carbon. Thus complexation may lead to a more selective reaction that may increase the yield of the desired ancillary ligands. Using this technique, selectivity is generally greater than about 50%, more preferably greater than about 70% and even more preferably greater than about 80%. Complexation may be particularly useful for the preparation of arrays of ancillary ligands of the type disclosed in the invention, where  $R^3$  is a variable in the preparation of the ancillary ligand array. As shown in Scheme 2 by the \*, where  $R^2$  and  $R^3$  are different, this approach also leads to the formation of a chiral center on the ancillary ligands of the invention. Under some circumstances  $R^3M^2$  may be successfully added to the imine in the absence the complexing reagent. Ancillary ligands that possess chirality may be important in certain olefin polymerization reactions, particularly those that lead to a stereospecific polymer, see "Stereospecific Olefin Polymerization with Chiral Metallocene Catalysts", Brintzinger, et al., *Angew. Chem. Int. Ed. Engl.*, 1995, Vol. 34, pp. 1143-1170, and the references therein; Bercaw et al., *J. Am. Chem. Soc.*, 1999, Vol. 121, 564-573; and Bercaw et al., *J. Am. Chem. Soc.*, 1996, Vol. 118, 11988-11989; each of which is

incorporated herein by reference.

[0078] In the practice of high throughput methods or combinatorial materials science, introduction of diversity may be important in designing libraries or arrays. The synthetic schemes discussed herein will allow those of skill in the art to introduce diversity on the  
5 ligands, which may assist in optimizing the selection of a particular ligand for a particular polymerization reaction. Step 1 (see Scheme1) may be conducted with, for example, any combination of the pyridines and anilines shown in Tables 1 and 2 (shown in Figures 1 and 2, respectively). The compounds shown in Tables 1 and 2 are meant to be illustrative and non-limiting.

10

### Compositions

[0079] Once the desired ligand is formed, it may be combined with a metal atom, ion, compound or other metal precursor compound. In some applications, the ligands of this invention will be combined with a metal compound or precursor and the product of such  
15 combination is not determined, if a product forms. For example, the ligand may be added to a reaction vessel at the same time as the metal or metal precursor compound along with the reactants, activators, scavengers, etc. Additionally, the ligand can be modified prior to addition to or after the addition of the metal precursor, e.g. through a deprotonation reaction or some other modification.

20 [0080] For formulas I, II, III, IV and V, the metal precursor compounds may be characterized by the general formula  $Hf(L)_n$  where L is independently selected from the group consisting of halide (F, Cl, Br, I), alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy,  
25 aryloxy, hydroxy, boryl, silyl, amino, amine, hydrido, allyl, diene, seleno, phosphino, phosphine, carboxylates, thio, 1,3-dionates, oxalates, carbonates, nitrates, sulphates, ethers, thioethers and combinations thereof; and optionally two or more L groups may be linked together in a ring structure. n is 1, 2, 3, 4, 5, or 6. The hafnium precursors may be  
30 typically contains some amount of impurity of zirconium. Thus, this invention uses as pure hafnium as is commercially reasonable. Specific examples of suitable hafnium precursors include, but are not limited to  $HfCl_4$ ,  $Hf(CH_2Ph)_4$ ,  $Hf(CH_2CMe_3)_4$ ,  $Hf(CH_2SiMe_3)_4$ ,  $Hf(CH_2Ph)_3Cl$ ,  $Hf(CH_2CMe_3)_3Cl$ ,  $Hf(CH_2SiMe_3)_3Cl$ ,  $Hf(CH_2Ph)_2Cl_2$ ,

$\text{Hf}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_2$ ,  $\text{Hf}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}_2$ ,  $\text{Hf}(\text{NMe}_2)_4$ ,  $\text{Hf}(\text{NEt}_2)_4$ , and  $\text{Hf}(\text{N}(\text{SiMe}_3)_2)_2\text{Cl}_2$ .

Lewis base adducts of these examples are also suitable as hafnium precursors, for example, ethers, amines, thioethers, phosphines and the like are suitable as Lewis bases. Specific examples include  $\text{HfCl}_4(\text{THF})_2$ ,  $\text{HfCl}_4(\text{SMe}_2)_2$  and  $\text{Hf}(\text{CH}_2\text{Ph})_2\text{Cl}_2(\text{OEt}_2)$ .

- 5 [0081] For formulas IV and V, the metal precursor compounds may be characterized by the general formula  $\text{M}(\text{L})_n$  where M is hafnium or zirconium and each L is independently selected from the group consisting of halide (F, Cl, Br, I), alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl,
- 10 alkoxy, aryloxy, hydroxy, boryl, silyl, amino, amine, hydrido, allyl, diene, seleno, phosphino, phosphine, carboxylates, thio, 1,3-dionates, oxalates, carbonates, nitrates, sulphates, ethers, thioethers and combinations thereof. Optionally two or more L groups may be linked together in a ring structure. n is 4, typically. It is well known that hafnium metal typically contains some amount of impurity of zirconium. Thus, this
- 15 invention uses as pure hafnium or zirconium as is commercially reasonable. Specific examples of suitable hafnium and zirconium precursors include, but are not limited to  $\text{HfCl}_4$ ,  $\text{Hf}(\text{CH}_2\text{Ph})_4$ ,  $\text{Hf}(\text{CH}_2\text{CMe}_3)_4$ ,  $\text{Hf}(\text{CH}_2\text{SiMe}_3)_4$ ,  $\text{Hf}(\text{CH}_2\text{Ph})_3\text{Cl}$ ,  $\text{Hf}(\text{CH}_2\text{CMe}_3)_3\text{Cl}$ ,  $\text{Hf}(\text{CH}_2\text{SiMe}_3)_3\text{Cl}$ ,  $\text{Hf}(\text{CH}_2\text{Ph})_2\text{Cl}_2$ ,  $\text{Hf}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_2$ ,  $\text{Hf}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}_2$ ,  $\text{Hf}(\text{NMe}_2)_4$ ,  $\text{Hf}(\text{NEt}_2)_4$ , and  $\text{Hf}(\text{N}(\text{SiMe}_3)_2)_2\text{Cl}_2$ ;  $\text{ZrCl}_4$ ,  $\text{Zr}(\text{CH}_2\text{Ph})_4$ ,  $\text{Zr}(\text{CH}_2\text{CMe}_3)_4$ ,  $\text{Zr}(\text{CH}_2\text{SiMe}_3)_4$ ,
- 20  $\text{Zr}(\text{CH}_2\text{Ph})_3\text{Cl}$ ,  $\text{Zr}(\text{CH}_2\text{CMe}_3)_3\text{Cl}$ ,  $\text{Zr}(\text{CH}_2\text{SiMe}_3)_3\text{Cl}$ ,  $\text{Zr}(\text{CH}_2\text{Ph})_2\text{Cl}_2$ ,  $\text{Zr}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_2$ ,  $\text{Zr}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}_2$ ,  $\text{Zr}(\text{NMe}_2)_4$ ,  $\text{Zr}(\text{NEt}_2)_4$ ,  $\text{Zr}(\text{NMe}_2)_2\text{Cl}_2$ ,  $\text{Zr}(\text{NEt}_2)_2\text{Cl}_2$ , and  $\text{Zr}(\text{N}(\text{SiMe}_3)_2)_2\text{Cl}_2$ . Lewis base adducts of these examples are also suitable as hafnium precursors, for example, ethers, amines, thioethers, phosphines and the like are suitable as Lewis bases. Specific examples include  $\text{HfCl}_4(\text{THF})_2$ ,  $\text{HfCl}_4(\text{SMe}_2)_2$  and
- 25  $\text{Hf}(\text{CH}_2\text{Ph})_2\text{Cl}_2(\text{OEt}_2)$ .

[0082] The ligand to metal precursor compound ratio is typically in the range of about 0.01:1 to about 100:1, more preferably in the range of about 0.1:1 to about 10:1.

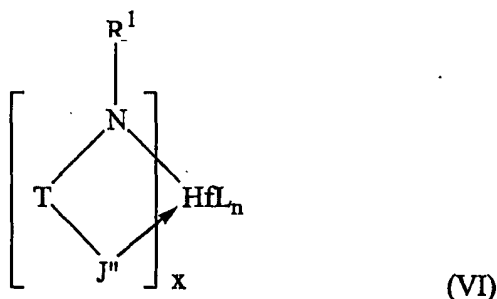
### Metal-Ligand Complexes

- 30 [0083] This invention, in part, relates to new metal-ligand complexes. Generally, the ligand is mixed with a suitable metal precursor compound prior to or simultaneously with allowing the mixture to be contacted with the reactants (e.g., monomers). When the ligand is mixed with the metal precursor compound, a metal-ligand complex may be

formed, which may be a catalyst or may need to be activated to be a catalyst. The metal-ligand complexes discussed herein are referred to as 2,1 complexes or 3,2 complexes, with the first number representing the number of coordinating atoms and second number representing the number of anionic sites on the ligand. The 2,1 complexes therefore

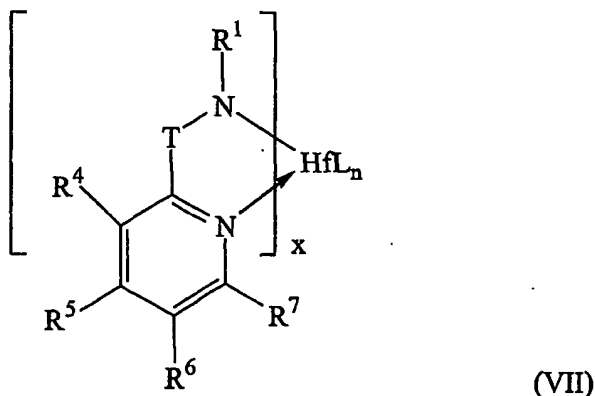
5 have two coordinating atoms and a single anionic charge. Other embodiments of this invention are those complexes that have a general 3,2 coordination scheme to a metal center, with 3,2 referring to a ligand that occupies three coordination sites on the metal and two of those sites being anionic and the remaining site being a neutral Lewis base type coordination.

- 10 [0084] Looking first at the 2,1 metal-ligand complexes, the metal-ligand complexes may be characterized by the following general formula:



wherein T, J'', R<sup>1</sup>, L and n are as defined previously; and x is 1 or 2. The J'' heteroaryl may or may not datively bond, but is drawn as bonding. More specifically, the metal-

- 15 ligand complexes may be characterized by the formula:

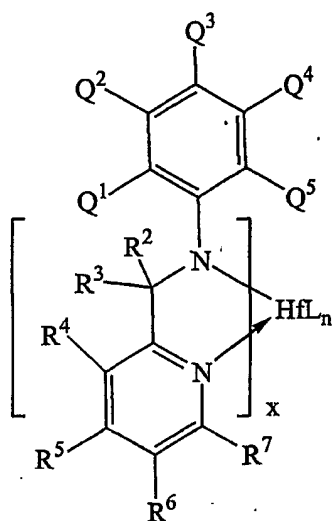


wherein R<sup>1</sup>, T, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, L and n are as defined previously; and x is 1 or 2. In one preferred embodiment x = 1 and n = 3. Additionally, Lewis base adducts of these metal-ligand complexes are also within the scope of the invention, for example, ethers, amines,

- 20 thioethers, phosphines and the like are suitable as Lewis bases.

[0085] More specifically, the metal-ligand complexes of this invention may be

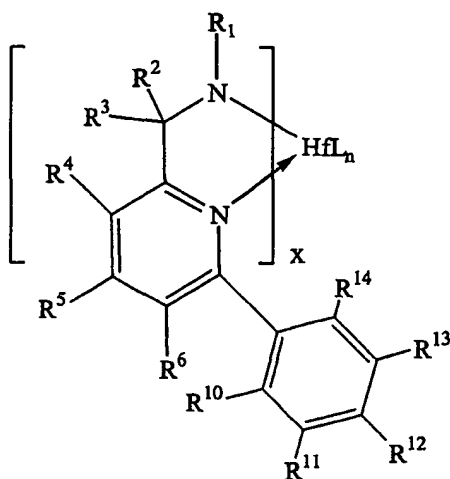
characterized by the general formula:



(VIII)

wherein the variables are generally defined above. Thus, e.g.,  $Q^2$ ,  $Q^3$ ,  $Q^4$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$  and  $R^7$  are independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxyl, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, nitro, and combinations thereof; optionally, two or more  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$  groups may be joined to form a fused ring system having from 3-50 non-hydrogen atoms in addition to the pyridine ring, e.g. generating a quinoline group; also, optionally, any combination of  $R^2$ ,  $R^3$  and  $R^4$  may be joined together in a ring structure;  $Q^1$  and  $Q^5$  are selected from the group consisting of alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, aryl, substituted aryl, provided that  $Q^1$  and  $Q^5$  are not both methyl; and each L is independently selected from the group consisting of halide, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, hydroxy, boryl, silyl, amino, amine, hydrido, allyl, diene, seleno, phosphino, phosphine, carboxylates, thio, 1,3-dionates, oxalates, carbonates, nitrates, sulphates, ethers, thioethers and combinations thereof; and optionally two L groups may be linked together in a ring structure; n is 1, 2, 3, 4, 5, or 6; and x = 1 or 2.

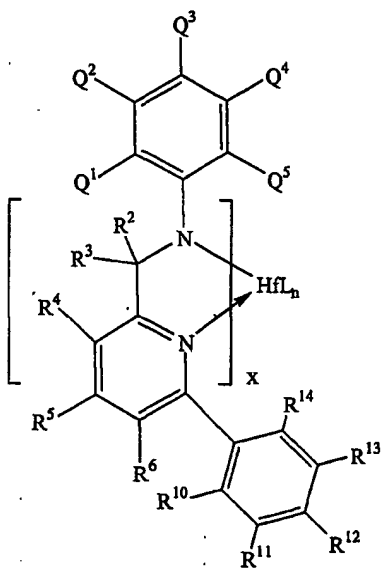
[0086] In other embodiments, the 2,1 metal-ligand complexes can be characterized by the general formula:



(IX)

wherein the variables are generally defined above.

[0087] In still other embodiments, the 2,1 metal-ligand complexes of this invention can be characterized by the general formula:

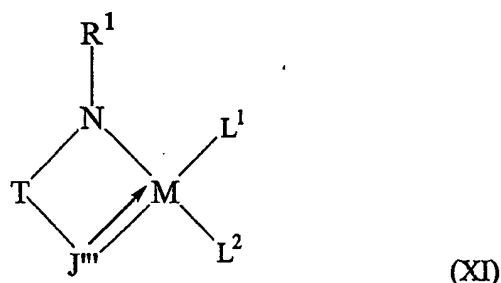


(X)

wherein the variables are generally defined above. The more specific embodiments of the metal-ligand complexes of formulas VI, VII, VIII, IX and X are explained above with regard to the specifics described for the ligands and metal precursors.

[0088] Lewis base adducts of these complexes are also suitable, for example, ethers, amines, thioethers, phosphines and the like are suitable as Lewis bases (note the definition of L).

[0089] Turning to the 3,2 metal-ligand complexes of this invention, the metal-ligand complexes in this aspect of this invention may be generally characterized by the general formula:

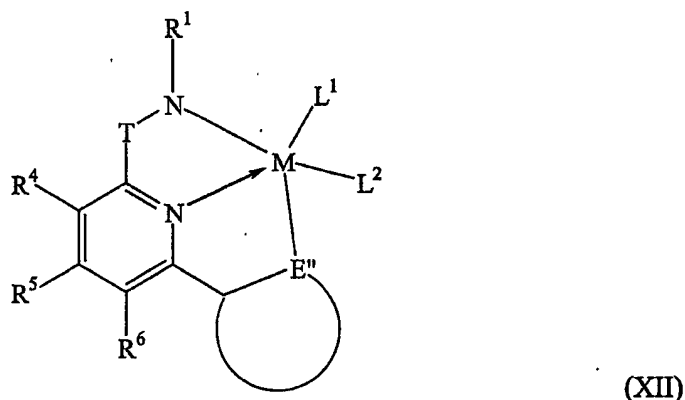


where M is zirconium or hafnium;

R<sup>1</sup> and T are defined above;

J''' being selected from the group of substituted heteroaryls with 2 atoms bonded  
 5 to the metal M, at least one of those 2 atoms being a heteroatom, and with one atom of  
 J''' is bonded to M via a dative bond, the other through a covalent bond; and  
 L<sup>1</sup> and L<sup>2</sup> are independently selected from the group consisting of halide, alkyl,  
 substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl,  
 heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl,  
 10 substituted heteroaryl, alkoxy, aryloxy, hydroxy, boryl, silyl, amino, amine, hydrido,  
 allyl, diene, seleno, phosphino, phosphine, carboxylates, thio, 1,3-dionates, oxalates,  
 carbonates, nitrates, sulphates, and combinations thereof; and optionally the L groups  
 may be linked together in a ring structure.

[0090] More specifically, the 3,2 metal-ligand complexes of this invention may be  
 15 characterized by the general formula:



where M is zirconium or hafnium;

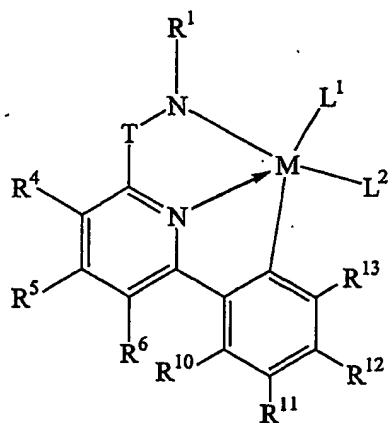
T, R<sup>1</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, L<sup>1</sup> and L<sup>2</sup> are defined above; and

E'' is either carbon or nitrogen and is part of an cyclic aryl, substituted aryl,  
 20 heteroaryl, or substituted heteroaryl group.

[0091] Even more specifically, the 3,2 metal-ligand complexes of this invention may be



characterized by the general formula:

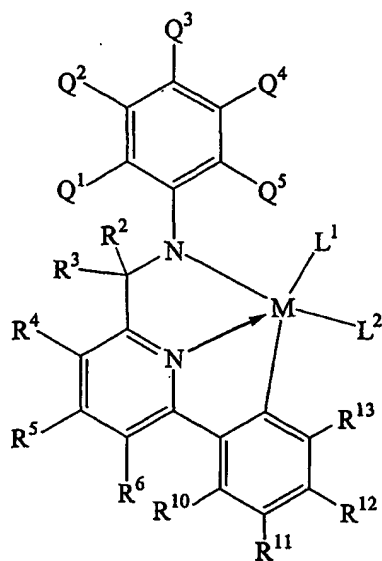


(XIII)

where M is zirconium or hafnium; and

T, R¹, R⁴, R⁵, R⁶, R¹⁰, R¹¹, R¹², R¹³, L¹ and L² are defined above.

- 5 [0092] Still even more specifically, the 3,2 metal-ligand complexes of this invention may be characterized by the general formula:



(XIV)

where M is zirconium or hafnium; and

T, R¹, R⁴, R⁵, R⁶, R¹⁰, R¹¹, R¹², R¹³, Q¹, Q², Q³, Q⁴, Q⁵, L¹ and L² are defined

10 above.

[0093] The more specific embodiments of the metal-ligand complexes of formulas XI, XII, XIII and XIV are explained above with regard to the specifics described for the ligands and metal precursors. Lewis base adducts of these complexes are also suitable, for example, ethers, amines, thioethers, phosphines and the like are suitable as Lewis

15 bases.

[0094] In addition, preferences for the substituents on the ligands for production of the particular polymers discussed above (*e.g.*, isotactic polypropylene) apply to the metal-ligand complexes just described. For isotactic polypropylene it is currently preferred that M is hafnium, although this preference is only slight as compared to zirconium. By  
5 "slight" here, it is meant that zirconium metal based polymerization of propylene for isotactic polypropylene shows similar tacticity control as compared to hafnium metal based polymerization, however, the hafnium based catalysts tend to show better polymerization activity and performance overall.

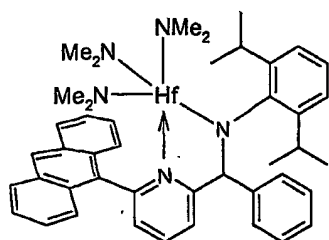
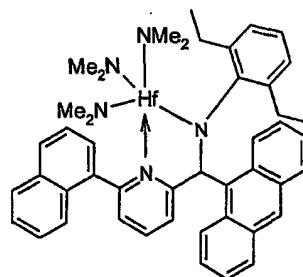
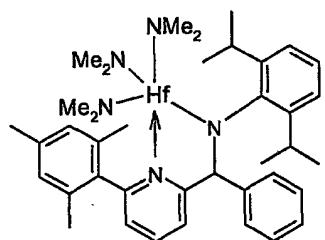
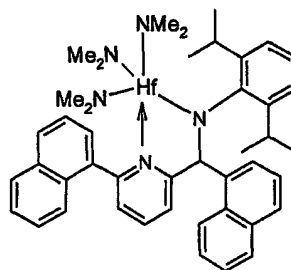
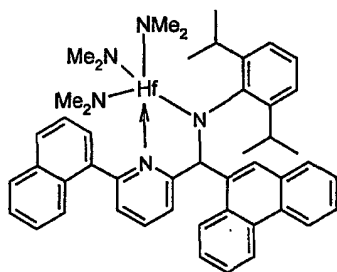
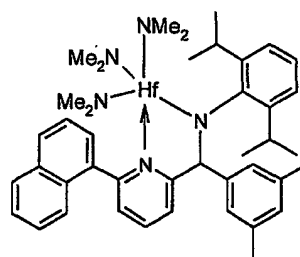
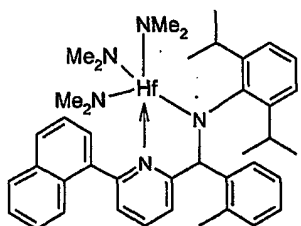
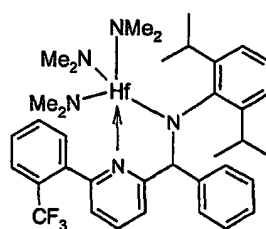
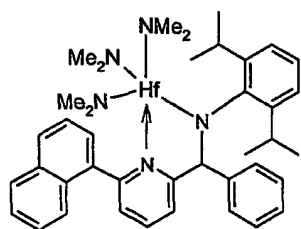
[0095] For isotactic polypropylene production, it is currently preferred that  $L^1$  and  $L^2$  are  
10 the same and selected from the group consisting of alkyl and dialkyl amino, more specifically from the group consisting of methyl and dimethylamino.

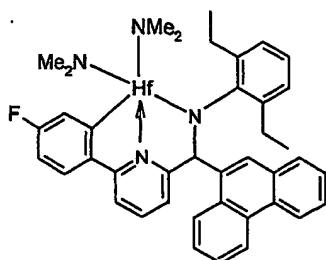
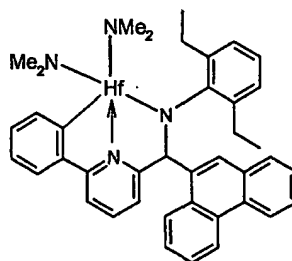
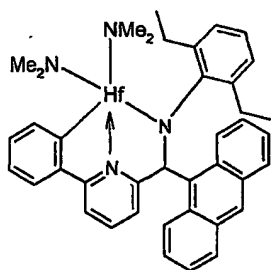
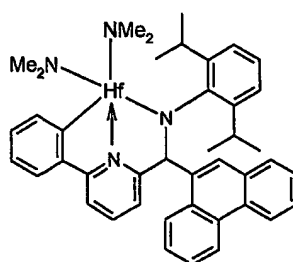
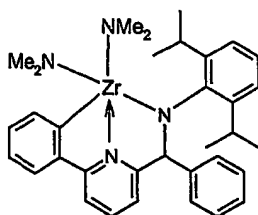
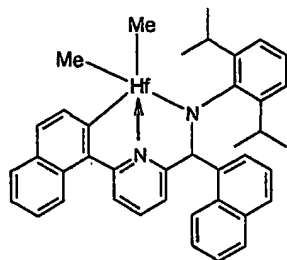
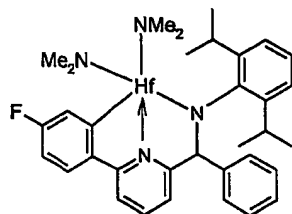
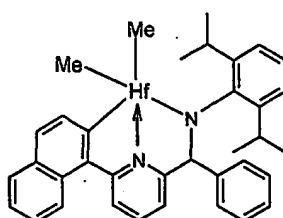
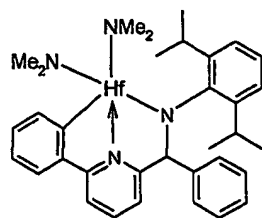
[0096] As above, for production of isotactic polypropylene,  $R^2$  and  $R^3$  are not the same group, leading to a chiral center on the carbon atom from which  $R^2$  and  $R^3$  stem. In more specific embodiments,  $R^2$  is hydrogen. In more specific embodiments for isotactic  
15 polypropylene production  $R^3$  is selected from the group consisting of hydrogen, halide, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, selenium, nitro, and combinations thereof. In more specific embodiments for isotactic  
20 polypropylene production  $R^3$  is aryl, substituted aryl, heteroaryl or substituted heteroaryl. In more specific embodiments for isotactic polypropylene production  $R^3$  is selected from the group consisting of benzyl, phenyl, 2-biphenyl, 2-dimethylaminophenyl, 2-methoxyphenyl, anthracenyl, mesityl, 2-pyridyl, 3,5-dimethylphenyl, o-tolyl and phenanthrenyl.

[0097] In the above formulas,  $R^{10}$ ,  $R^{11}$ ,  $R^{12}$  and  $R^{13}$  are independently selected from the  
25 group consisting of hydrogen, halide, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, selenium, nitro, and combinations thereof; optionally,  
30 two or more  $R^{10}$ ,  $R^{11}$ ,  $R^{12}$  and  $R^{13}$  groups may be joined to form a fused ring system having from 3-50 non-hydrogen atoms. Particular embodiments include, for example, for isotactic polypropylene production, it is currently preferred that  $R^{10}$ ,  $R^{11}$ ,  $R^{12}$ ,  $R^{13}$ , are each hydrogen; or one or more of  $R^{10}$ ,  $R^{11}$ ,  $R^{12}$ ,  $R^{13}$  are methyl, fluoro, trifluoromethyl,

methoxy, or dimethylamino; or where  $R^{10}$  and  $R^{11}$  are joined to form a benzene ring and  $R^{12}$  and  $R^{13}$  are each hydrogen (thus forming a naphthyl group with the existing phenyl ring).

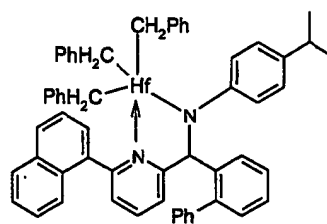
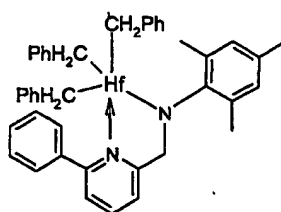
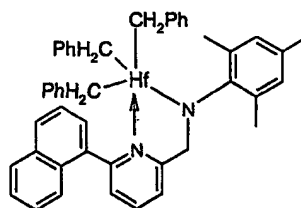
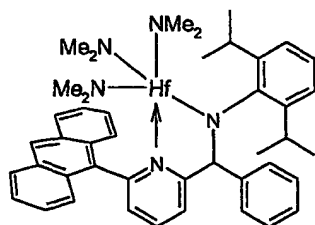
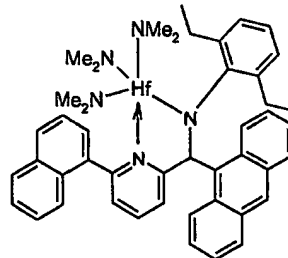
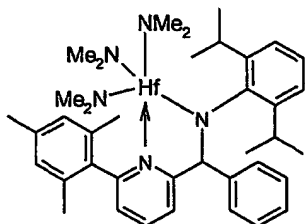
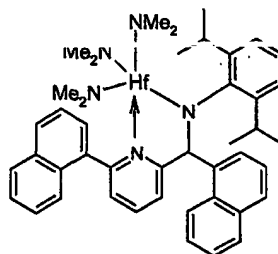
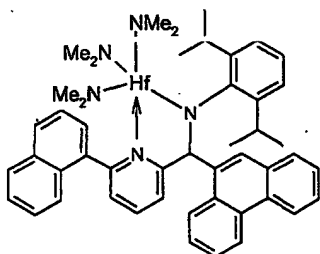
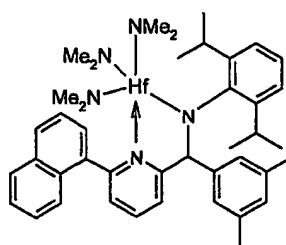
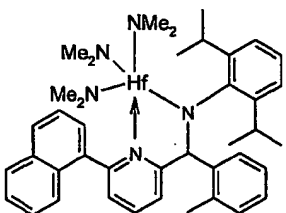
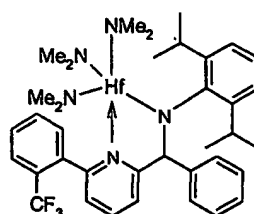
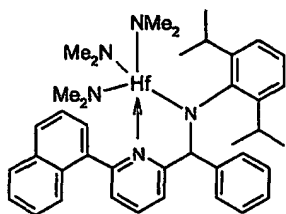
- [0098] Specific 2,1 and 3,2 metal complexes that are useful for the production of  
5 isotactic polypropylene include:

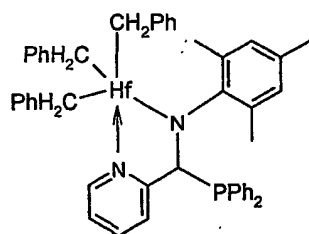
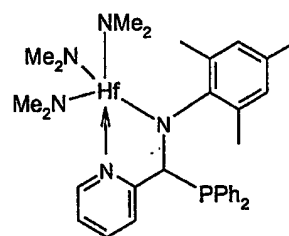
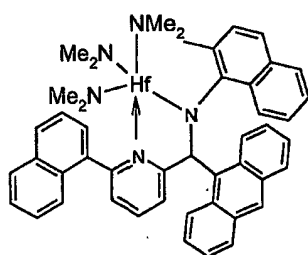
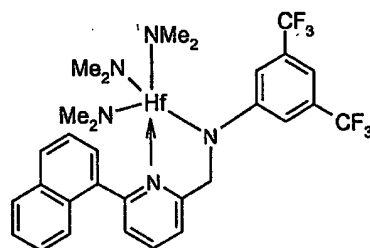
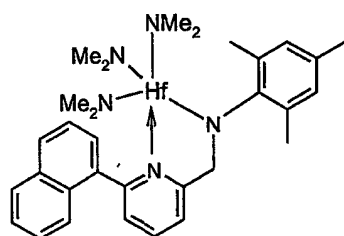
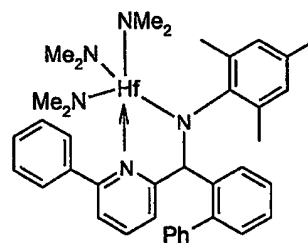
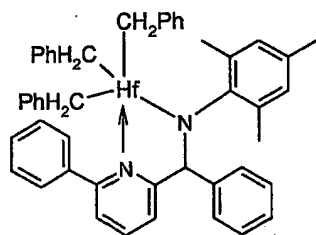
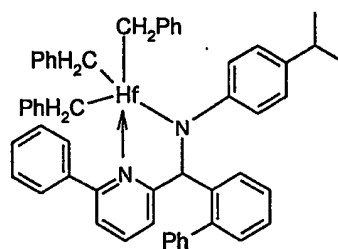
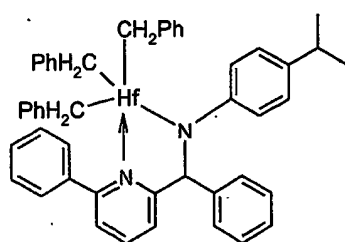




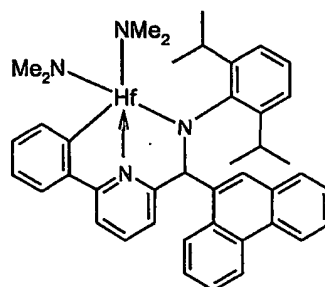
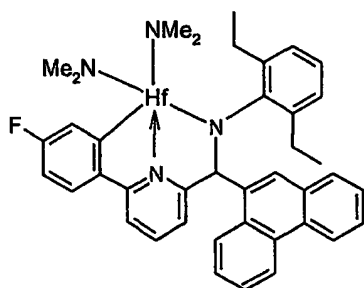
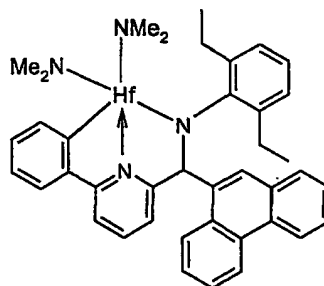
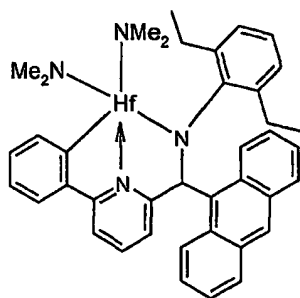
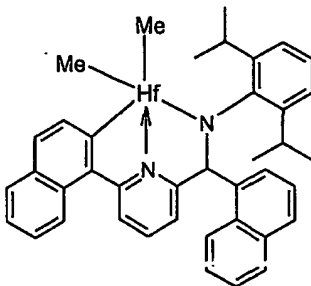
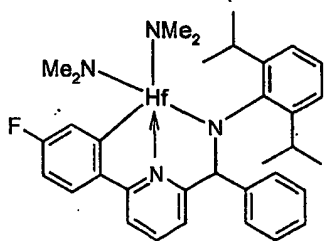
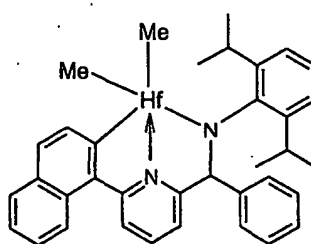
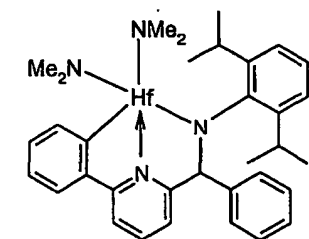
[0099] For the production of ethylene-styrene copolymers, there are different preferences depending on the type of polymer that is desired. In some embodiments, it is preferred that the above formulas for complexes are used, particularly with  $R^7$  selected from the

group consisting of aryl, substituted aryl, heteroaryl, and substituted heteroaryl. Specific 2,1 and 3,2 complexes that are preferred for ethylene-styrene copolymer production include:

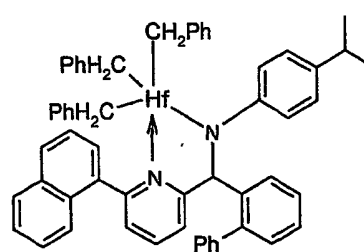
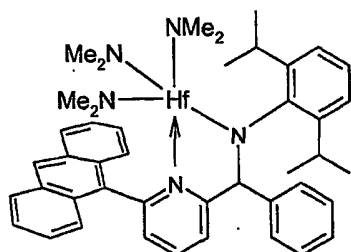
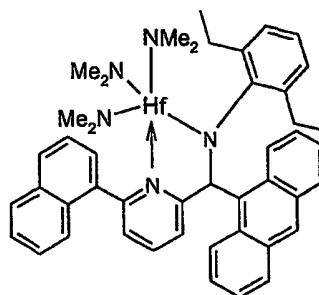
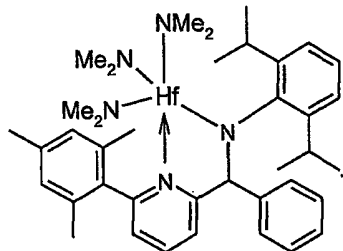
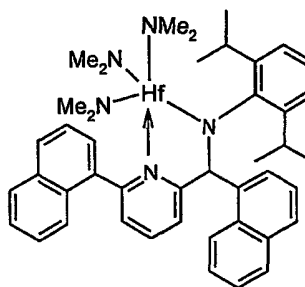
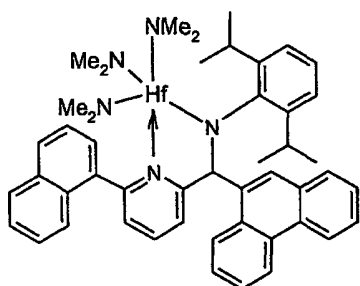
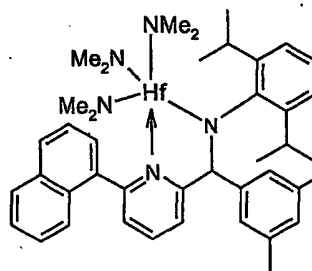
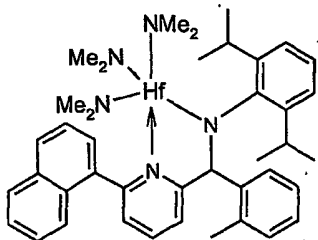
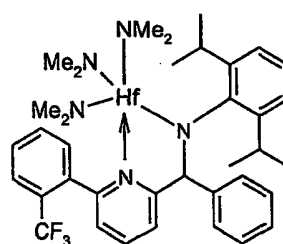
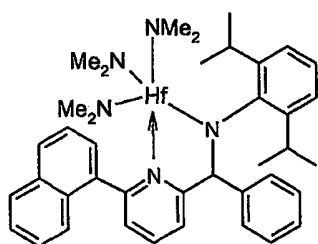


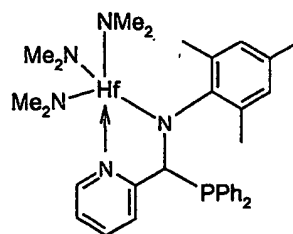
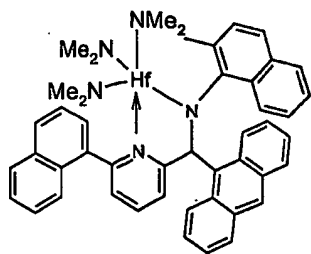
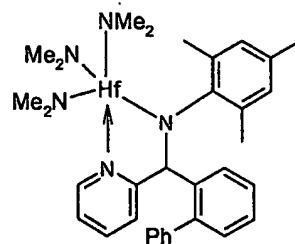
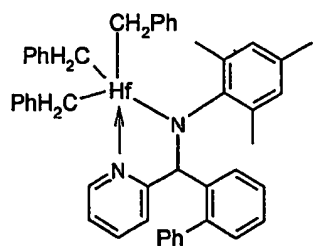
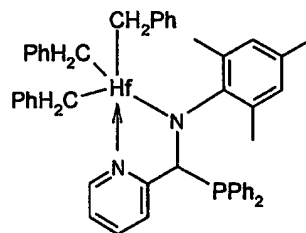
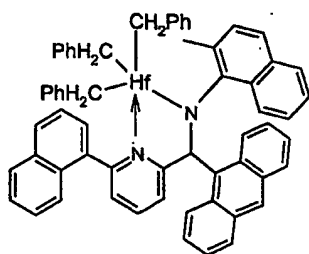
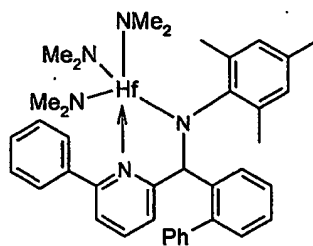
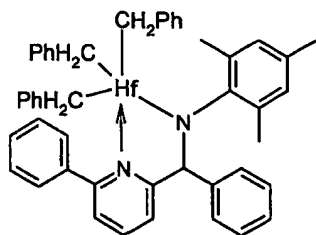
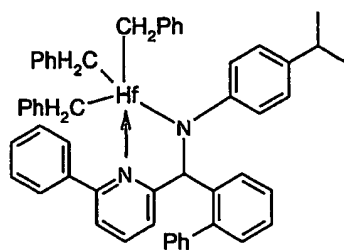
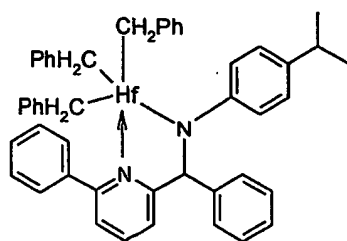


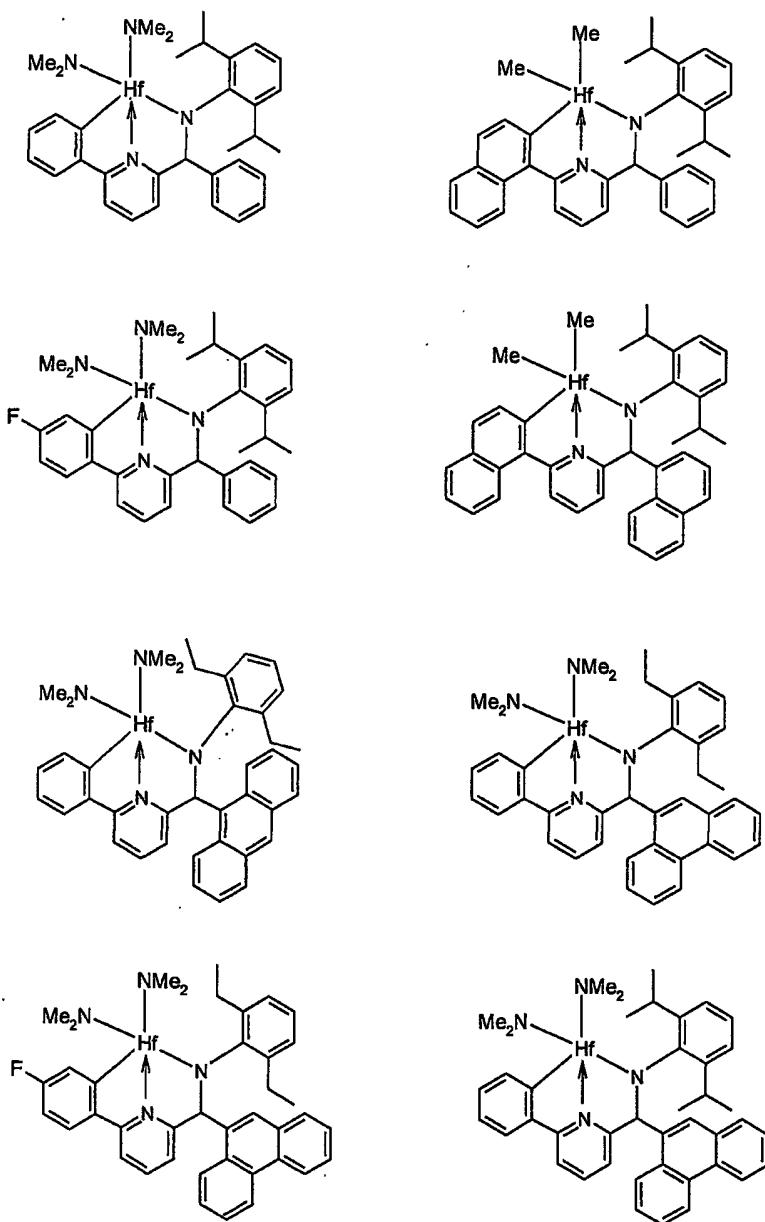




[0100] For the production of ethylene-1-octene copolymers, it is preferred that the metal complexes of the above general formulas are used, with either or both of  $R^3$  and/or  $R^7$  being independently selected from the group consisting of aryl, substituted aryl, heteroaryl, and substituted heteroaryl. Specific 2,1 and 3,2 metal complexes that are preferred for ethylene-1-octene copolymer production include:



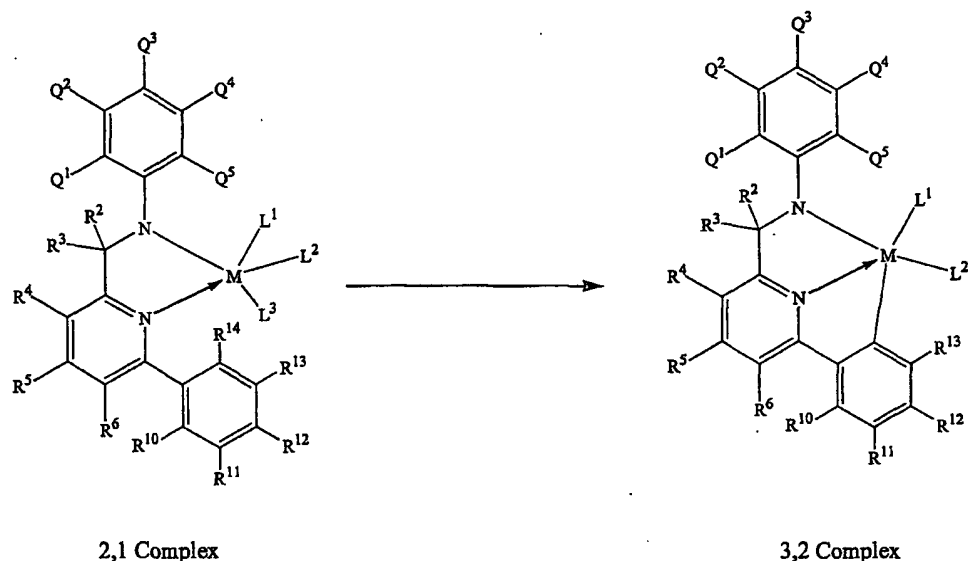




[0101] In addition, Lewis base adducts of the metal-ligand complexes in the above formulas are also suitable, for example, ethers, amines, thioethers, phosphines and the like are suitable as Lewis bases.

[0102] The metal-ligand complexes can be formed by techniques known to those of skill in the art, such as combinations of metal precursors and ligands under conditions to afford complexation. In some embodiments, R<sup>14</sup> is hydrogen and the metal-ligand complexes are formed by a metallation reaction (*in situ* or not) as shown below in

scheme 3:



Scheme 3

[0103] In scheme 3,  $R^{14}$  is hydrogen (but see above for the full definition of  $R^{14}$  in other embodiments of this invention). The metallation reaction to convert the 2,1 complex on the left to the 3,2 complex on the right can occur via a number of mechanisms, likely depending on the substituents chosen for  $L^1$ ,  $L^2$  and  $L^3$  and the other substituents such as  $Q^1$ - $Q^5$ ,  $R^2$ - $R^6$ ,  $R^{10}$  to  $R^{13}$ . In one embodiment, when  $L^1$ ,  $L^2$  and  $L^3$  are each  $N(CH_3)_2$ , the reaction can proceed by heating the 2,1 complex to a temperature above about  $100^\circ C$ . In this embodiment, it is believed that  $L^1$  and  $L^2$  remain  $N(CH_3)_2$  in the 3,2 complex. In another embodiment when  $L^1$ ,  $L^2$  and  $L^3$  are each  $N(CH_3)_2$ , the reaction can proceed by adding a group 13 reagent (as described below) to the 2,1 complex at a suitable temperature (such as room temperature). Preferably the group 13 reagent for this purpose is di-isobutyl aluminum hydride, tri-isobutyl aluminum or trimethyl aluminum.

In this embodiment,  $L^1$  and  $L^2$  are typically converted to the ligand (e.g., alkyl or hydride) stemming from the group 13 reagent (e.g., from trimethyl aluminum,  $L^1$  and  $L^2$  are each  $CH_3$  in the 3,2 complex). The 2,1 complex in scheme 3 is formed by the methods discussed above.

[0104] In an alternative embodiment possibly outside the scope of scheme 3, for isotactic polypropylene production, it is currently preferred that  $R^{14}$  is either hydrogen or methyl.

[0105] Various references disclose metal complexes that may appear to be similar; see for example, U.S. 6,103, 657 and U.S. 5,637,660, both of which are incorporated herein by reference for all purposes. However, certain embodiments of the invention herein

provide unexpectedly improved polymerization performance (e.g., higher activity and/or higher polymerization temperatures and/or higher comonomer incorporation) relative to the embodiments disclosed in those references. In particular, as shown in certain of the examples herein, the activity of the hafnium metal catalysts is far superior to that of the zirconium catalysts. Indeed, it also appears as if the zirconium metal centered catalysts have inferior performance with respect to incorporation of comonomer into an ethylene/comonomer type copolymer, especially for 1-octene, isobutylene and styrene comonomers.

[0106] The ligands, complexes or catalysts may be supported on an organic or inorganic support. Suitable supports include silicas, aluminas, clays, zeolites, magnesium chloride, polyethyleneglycols, polystyrenes, polyesters, polyamides, peptides and the like. Polymeric supports may be cross-linked or not. Similarly, the ligands, complexes or catalysts may be supported on similar supports known to those of skill in the art. In addition, the catalysts of this invention may be combined with other catalysts in a single reactor and/or employed in a series of reactors (parallel or serial) in order to form blends of polymer products.

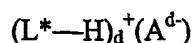
#### Polymerization Activators/Additives

[0107] The metal-ligand complexes and compositions are active catalysts typically in combination with a suitable activator, combination of activators, activating technique or activating package, although some of the ligand-metal complexes may be active without an activator or activating technique. Broadly, the activator(s) may comprise alumoxanes, Lewis acids, Bronsted acids, compatible non-interfering activators and combinations of the foregoing. These types of activators have been taught for use with different compositions or metal complexes in the following references, which are hereby incorporated by reference in their entirety: U.S. Patents 5,599,761, 5,616,664, 5,453,410, 5,153,157, 5,064,802, and EP-A-277,004. In particular, ionic or ion forming activators are preferred.

[0108] Suitable ion forming compounds useful as an activator in one embodiment of the present invention comprise a cation that is a Bronsted acid capable of donating a proton, and an inert, compatible, non-interfering, anion, A<sup>-</sup>. Preferred anions are those containing a single coordination complex comprising a charge-bearing metal or metalloid core. Mechanistically, said anion should be sufficiently labile to be displaced

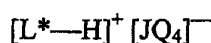
by olefinic, diolefinic and unsaturated compounds or other neutral Lewis bases such as ethers or nitriles. Suitable metals include, but are not limited to, aluminum, gold and platinum. Suitable metalloids include, but are not limited to, boron, phosphorus, and silicon. Compounds containing anions that comprise coordination complexes containing a single metal or metalloid atom are, of course, well known and many, particularly such compounds containing a single boron atom in the anion portion, are available commercially.

[0109] Preferably such activators may be represented by the following general formula:



wherein,  $L^*$  is a neutral Lewis base;  $(L^*-H)^+$  is a Bronsted acid;  $A^{d-}$  is a non-interfering, compatible anion having a charge of  $d-$ , and  $d$  is an integer from 1 to 3. More preferably  $A^{d-}$  corresponds to the formula:  $[M^{3+} Q_h]^{d-}$  wherein  $h$  is an integer from 4 to 6;  $h-3 = d$ ;  $M'$  is an element selected from Group 13 of the Periodic Table of the Elements; and  $Q$  is independently selected from the group consisting of hydride, dialkylamido, halide, alkoxide, aryloxy, hydrocarbyl, and substituted-hydrocarbyl radicals (including halidesubstituted hydrocarbyl, such as perhalogenated hydrocarbyl radicals), said  $Q$  having up to 20 carbons. In a more preferred embodiment,  $d$  is one, i.e., the counter ion has a single negative charge and corresponds to the formula  $A^-$ .

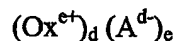
[0110] Activators comprising boron or aluminum which are particularly useful in the preparation of catalysts of this invention may be represented by the following general formula:



wherein:  $L^*$  is as previously defined;  $J$  is boron or aluminum; and  $Q$  is a fluorinated  $C_{1-20}$  hydrocarbyl group. Most preferably,  $Q$  is independently selected from the group selected from the group consisting of fluorinated aryl group, especially, a pentafluorophenyl group (i.e., a  $C_6F_5$  group) or a 3,5-bis( $CF_3$ ) $_2C_6H_3$  group. Illustrative, but not limiting, examples of boron compounds which may be used as an activating cocatalyst in the preparation of the improved catalysts of this invention are tri-substituted ammonium salts such as: trimethylammonium tetraphenylborate, triethylammonium tetraphenylborate, tripropylammonium tetraphenylborate, tri(n-butyl)ammonium tetraphenylborate, tri(t-butyl)ammonium tetraphenylborate, N,N-dimethylanilinium tetraphenylborate, N,N-diethylanilinium tetraphenylborate, N,N-dimethylanilinium tetra-(3,5-bis(trifluoromethyl)phenyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium)

tetraphenylborate, trimethylammonium tetrakis(pentafluorophenyl) borate, triethylammonium tetrakis(pentafluorophenyl) borate, tripropylammonium tetrakis(pentafluorophenyl) borate, tri(n-butyl)ammonium tetrakis(pentafluorophenyl) borate, tri(secbutyl)ammonium tetrakis(pentafluorophenyl) borate, N,N-dimethylanilinium tetrakis(pentafluorophenyl) borate, N,N-diethylanilinium tetrakis(pentafluorophenyl) borate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(pentafluorophenyl) borate, trimethylammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate and N,N-dimethylanilinium tetrakis-(2,3,4,6-tetrafluorophenyl) borate; dialkyl ammonium salts such as: di-(i-propyl)ammonium tetrakis(pentafluorophenyl) borate, and dicyclohexylammonium tetrakis(pentafluorophenyl) borate; and tri-substituted phosphonium salts such as: triphenylphosphonium tetrakis(pentafluorophenyl) borate, tri(o-tolyl)phosphonium tetrakis(pentafluorophenyl) borate, and tri(2,6-dimethylphenyl)phosphonium tetrakis(pentafluorophenyl) borate; and N,N-dimethylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate. Preferred  $[L^* - H]^+$  cations are N,N-dimethylanilinium and tributylammonium. Preferred anions are tetrakis(3,5-bis(trifluoromethyl)phenyl)borate and tetrakis(pentafluorophenyl)borate. In some embodiments, the most preferred activator is  $PhNMe_2H^+B(C_6F_5)_4^-$ .

[0111] Other suitable ion forming activators comprise a salt of a cationic oxidizing agent and a non-interfering, compatible anion represented by the formula:



wherein:  $Ox^{e+}$  is a cationic oxidizing agent having a charge of  $e+$ ;  $e$  is an integer from 1 to 3; and  $A^{d-}$ , and  $d$  are as previously defined. Examples of cationic oxidizing agents include: ferrocenium, hydrocarbyl-substituted ferrocenium,  $Ag^+$ , or  $Pb^{+2}$ . Preferred embodiments of  $A^{d-}$  are those anions previously defined with respect to the Bronsted acid containing activating cocatalysts, especially tetrakis(pentafluorophenyl)borate.

[0112] Another suitable ion forming, activating cocatalyst comprises a compound that is a salt of a carbenium ion or silyl cation and a non-interfering, compatible anion represented by the formula:



wherein:  $C^+$  is a  $C_{1-100}$  carbenium ion or silyl cation; and  $A^-$  is as previously defined. A preferred carbenium ion is the trityl cation, i.e. triphenylcarbenium. The silyl cation may be characterized by the formula  $Z^1Z^2Z^3Si^+$  cation, where each of  $Z^1$ ,  $Z^2$ , and  $Z^3$  is



independently selected from the group consisting of alkyl, substituted alkyl, cycloalkyl, heterocycloalkyl, heterocyclic, aryl, substituted aryl, heteroaryl, substituted heteroaryl and combinations thereof. In some embodiments, a most preferred activator is  $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ .

- 5 [0113] Other suitable activating cocatalysts comprise a compound that is a salt, which is represented by the formula  $(\text{A}^{*+a})_b(\text{Z}^*\text{J}^*_j)^{-c}_d$  wherein  $\text{A}^*$  is a cation of charge  $+a$ ;  $\text{Z}^*$  is an anion group of from 1 to 50, preferably 1 to 30 atoms, not counting hydrogen atoms, further containing two or more Lewis base sites;  $\text{J}^*$  independently each occurrence is a Lewis acid coordinated to at least one Lewis base site of  $\text{Z}^*$ , and optionally two or more
- 10 such  $\text{J}^*$  groups may be joined together in a moiety having multiple Lewis acidic functionality;  $j$  is a number from 2 to 12; and  $a$ ,  $b$ ,  $c$ , and  $d$  are integers from 1 to 3, with the proviso that  $a \times b$  is equal to  $c \times d$ . See, WO 99/42467, which is incorporated herein by reference. In other embodiments, the anion portion of these activating cocatalysts may be characterized by the formula  $((\text{C}_6\text{F}_5)_3\text{M}^{\text{'''}}} \text{--} \text{LN} \text{--} \text{M}^{\text{'''}}}(\text{C}_6\text{F}_5)_3)^-$  where  $\text{M}^{\text{'''}}$  is boron
- 15 or aluminum and LN is a linking group, which is preferably selected from the group consisting of cyanide, azide, dicyanamide and imidazolidine. The cation portion is preferably a quaternary amine. See, e.g., LaPointe, *et al.*, *J. Am. Chem. Soc.* **2000**, 122, 9560-9561, which is incorporated herein by reference.

- [0114] In addition, suitable activators include Lewis acids, such as those selected from
- 20 the group consisting of tris(aryl)boranes, tris(substituted aryl)boranes, tris(aryl)alanes, tris(substituted aryl)alanes, including activators such as tris(pentafluorophenyl)borane. Other useful ion forming Lewis acids include those having two or more Lewis acidic sites, such as those described in WO 99/06413 or Piers, *et al.* "New Bifunctional Perfluoroaryl Boranes: Synthesis and Reactivity of the *ortho*-Phenylene-Bridged
- 25 Diboranes 1,2- $[\text{B}(\text{C}_6\text{F}_5)_2]_2\text{C}_6\text{X}_4$  ( $\text{X} = \text{H}, \text{F}$ )", *J. Am. Chem. Soc.*, **1999**, 121, 3244-3245, both of which are incorporated herein by reference. Other useful Lewis acids will be evident to those of skill in the art. In general, the group of Lewis acid activators is within the group of ion forming activators (although exceptions to this general rule can be found) and the group tends to exclude the group 13 reagents listed below.

- 30 Combinations of ion forming activators may be used.

[0115] Other general activators or compounds useful in a polymerization reaction may be used. These compounds may be activators in some contexts, but may also serve other functions in the polymerization system, such as alkylating a metal center or scavenging

impurities. These compounds are within the general definition of "activator," but are not considered herein to be ion-forming activators. These compounds include a group 13 reagent that may be characterized by the formula  $G^{13}R'_{3-p}D_p$  where  $G^{13}$  is selected from the group consisting of B, Al, Ga, In and combinations thereof, p is 0, 1 or 2, each R' is independently selected from the group consisting of alkyl, substituted alkyl, cycloalkyl, heterocycloalkyl, heterocyclic and combinations thereof, and each D is independently selected from the group consisting of halide, hydride, alkoxy, aryloxy, amino, thio, phosphino and combinations thereof. In other embodiments, the group 13 activator is an oligomeric or polymeric alumoxane compound, such as methylalumoxane and the known modifications thereof. In other embodiments, a divalent metal reagent may be used that is defined by the general formula  $M'R'_{2-p}D_p$ , and p' is 0 or 1 in this embodiment and R' and D are as defined above. M' is the metal and is selected from the group consisting of Mg, Ca, Sr, Ba, Zn, Cd and combinations thereof. In still other embodiments, an alkali metal reagent may be used that is defined by the general formula  $M''R'$  and in this embodiment R' is as defined above. M'' is the alkali metal and is selected from the group consisting of Li, Na, K, Rb, Cs and combinations thereof. Additionally, hydrogen and/or silanes may be used in the catalytic composition or added to the polymerization system. Silanes may be characterized by the formula  $SiR'_{4-q}D_q$  where R' is defined as above, q is 1, 2, 3 or 4 and D is as defined above, with the proviso that there is at least one D that is a hydride.

[0116] The molar ratio of metal:activator (whether a composition or complex is employed as a catalyst) employed preferably ranges from 1:10,000 to 100:1, more preferably from 1:5000 to 10:1, most preferably from 1:10 to 1:1. In a preferred embodiment of the invention mixtures of the above compounds are used, particularly a combination of a group 13 reagent and an ion-forming activator. The molar ratio of group 13 reagent to ion-forming activator is preferably from 1:10,000 to 1000:1, more preferably from 1:5000 to 100:1, most preferably from 1:100 to 100:1. In a preferred embodiment, the ion forming activators are combined with a tri-alkyl aluminum, specifically trimethylaluminum, triethylaluminum, tri-n-octylaluminum, or triisobutylaluminum or with a di-alkyl aluminum hydride such as di-isobutyl aluminum hydride. A most preferred combination is about 1 equivalent of N,N-dimethylanilinium tetrakis(pentafluorophenyl) borate, and 5-30 equivalents of a Group 13 reagent. For ethylene-isobutylene copolymerization the group 13 reagent should be present in at least

an amount that is 0.1 equivalents of the metal (*e.g.*, the metal precursor compound) and preferably in an amount that is between 1 and 10 equivalents of the metal.

[0117] In other applications, the ligand will be mixed with a suitable metal precursor compound prior to or simultaneous with allowing the mixture to be contacted to the  
5 reactants. When the ligand is mixed with the metal precursor compound, a metal-ligand complex may be formed, which may be a catalyst. In connection with the metal-ligand complex and depending on the ligand or ligands chosen, the metal-ligand complex may take the form of dimers, trimers or higher orders thereof or there may be two or more metal atoms that are bridged by one or more ligands. Furthermore, two or more ligands  
10 may coordinate with a single metal atom. The exact nature of the metal-ligand complex(es) or compound(s) formed depends on the chemistry of the ligand and the method of combining the metal precursor and ligand, such that a distribution of metal-ligand complexes may form with the number of ligands bound to the metal being greater or less than the number of equivalents of ligands added relative to an equivalent of metal  
15 precursor.

#### Monomers/Polymers

[0118] The compositions, complexes and/or catalysts of this invention are particularly effective at polymerizing  $\alpha$ -olefins (such as propylene, 1-butene, 1-pentene, 1-hexene,  
20 1-heptene, 1-octene, and styrene), copolymerizing ethylene with  $\alpha$ -olefins (such as propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, and styrene), and copolymerizing ethylene with 1,1-disubstituted olefins (such as isobutylene). These compositions might also polymerize monomers that have polar functionalities in homopolymerizations or copolymerizations and/or homopolymerize 1,1-disubstituted  
25 olefins. Also, diolefins in combination with ethylene and/or  $\alpha$ -olefins or 1,1-disubstituted olefins may be copolymerized. The new catalyst compositions can be prepared by combining a metal precursor with a suitable ligand and, optionally, an activator or combination of activators.

[0119] In general monomers useful herein may be olefinically or unsaturated monomers  
30 having from 2 to 20 carbon atoms either alone or in combination. Generally, monomers may include olefins, diolefins and unsaturated monomers including ethylene and  $C_3$  to  $C_{20}$   $\alpha$ -olefins such as propylene, 1-butene, 1-hexene, 1-octene, 4-methyl-1-pentene, 1-norbornene, styrene and mixtures thereof; additionally, 1,1-disubstituted olefins, such as

isobutylene, 2-methyl-1-butene, 2-methyl-1-pentene, 2-ethyl-1-pentene, 2-methyl-1-hexene, 3-trimethylsilyl-2-methyl-1-propene,  $\alpha$ -methyl-styrene, either alone or with other monomers such as ethylene or  $C_3$  to  $C_{20}$   $\alpha$ -olefins and/or diolefins. The  $\alpha$ -olefins listed above may be polymerized in a stereospecific manner e.g. to generate isotactic or syndiotactic or hemiisotactic polypropylene. Additionally the  $\alpha$ -olefins may be polymerized to produce a polymer with differing tacticity sequences within the polymer chain, such as polypropylene containing atactic and isotactic sequences within the same polymer chain. These definitions are intended to include cyclic olefins. Diolefins generally comprise 1,3-dienes such as (butadiene), substituted 1,3-dienes (such as isoprene) and other substituted 1,3-dienes, with the term substituted referring to the same types of substituents referred to above in the definition section. Diolefins also comprises 1,5-dienes and other non-conjugated dienes. The styrene monomers may be unsubstituted or substituted at one or more positions on the aryl ring. The use of diolefins in this invention is typically in conjunction with another monomer that is not a diolefin. In some embodiments, acetylenically unsaturated monomers may be employed.

[0120] More specifically, it has been found that the catalysts of the present invention are particularly active for certain monomers, particularly  $\alpha$ -olefins. Thus, the catalysts of the present invention may provide higher comonomer incorporation for copolymers of ethylene and co-monomers having three or more carbon atoms.

[0121] In addition, the catalysts of the present invention may polymerize vinyl chloride alone (e.g., in a homopolymerization) or with other monomers (such as ethylene or  $C_3$  to  $C_{20}$   $\alpha$ -olefins). Furthermore, vinyl monomers with functional groups may also be polymerized alone (e.g., in a homopolymerization) or with other monomers (such as ethylene or  $C_3$  to  $C_{20}$   $\alpha$ -olefins). Such functional group containing vinyl monomers can be characterized by the general formula  $H_2C=CH-FG$ , where FG is the functional group that contains at least one heteroatom (using the previous definition) or halogen (e.g., Cl, F, Br, etc.). Functional monomers include  $C_1$ - $C_{20}$  acrylates,  $C_1$ - $C_{20}$  methacrylates,  $C_1$ - $C_{20}$  vinylacetates, acrylic acid, methacrylic acid, maleic anhydride, vinyl acetate, vinyl ethers, acrylonitrile, acrylamide, vinyl chloride and mixtures thereof.

[0122] Novel polymers, copolymers or interpolymers may be formed having unique physical and/or melt flow properties. Such novel polymers can be employed alone or with other polymers in a blend to form products that may be molded, cast, extruded or spun. End uses for the polymers made with the catalysts of this invention include films

for packaging, trash bags, bottles, containers, foams, coatings, insulating devices and household items. Also, such functionalized polymers are useful as solid supports for organometallic or chemical synthesis processes.

[0123] More specifically, the catalysts of this invention have prepared novel copolymers  
5 of ethylene and isobutylene. These novel polymers have high molecular weight combined with high incorporation of isobutylene. Others have broadly claimed such copolymers. See e.g., U.S. Patents 5,866,665 and 5,763,556, which are both incorporated herein by reference. However, the combination of these properties has not been previously exemplified and is commercially promising. More specifically, the  
10 novel copolymers have a number average molecular weight of at least 50,000 and a weight percent incorporation of isobutylene of at least about 30 wt.%.

[0124] Also, it has been found that the catalytic performance at high temperature of particular catalysts of the present invention for the polymerization of olefins in general, including the co-polymerization of ethylene and  $\alpha$ -olefins, is unexpectedly good. In  
15 particular, it has been found that varying the ligand substituents (R and Q groups) discussed herein allows one to increase the polymerization performance and polymer molecular weight for olefin polymerizations at high temperatures, particularly for polymerization temperatures above 120°C. In particular, when R<sup>3</sup> is aryl or substituted aryl, the high temperature polymerization catalytic performance is improved compared to  
20 when R<sup>3</sup> is hydrogen or alkyl. Also, the steric bulk of the R<sup>1</sup> and R<sup>7</sup> groups can affect polymerization performance. In particular, improved high temperature polymerization performance is observed when Q<sup>1</sup> and Q<sup>5</sup> are both not hydrogen.

[0125] It has been found that particular catalysts of the present invention co-polymerize ethylene and styrene (or substituted styrenes), forming ethylene-styrene copolymers. In  
25 particular, it has been found that varying the ligand substituents (R and Q groups) discussed herein allows one to vary the ratio of styrene to ethylene incorporated in the copolymer, and the ethylene-styrene copolymerization activity and Mw of the resulting ethylene-styrene copolymer. In particular, when R<sup>7</sup> is aryl or substituted aryl, the ratio of styrene to ethylene incorporated in the copolymer is significantly higher than when R<sup>7</sup> is  
30 hydrogen or alkyl. The higher level of styrene incorporation when R<sup>7</sup> is aryl or substituted aryl is unexpected.

[0126] The  $\alpha$ -olefins listed above may be polymerized in a stereospecific manner e.g. to generate isotactic or syndiotactic or hemiisotactic poly-  $\alpha$  -olefins. Additionally the

$\alpha$ -olefins may be polymerized to produce a polymer with differing tacticity sequences within the polymer chain, such as polypropylene containing atactic and isotactic sequences within the same polymer chain. The stereoregularity may be interrupted by stereoerrors, in particular isolated stereoerrors have been observed, which is an indication of enantiomorphic side control. Also regioerrors might be present in the isotactic polypropylene polymer as it is described in the literature. In particular isolated 2-1 insertions may be observed. (see, e.g., Resconi et al., "Selectivity in Propene Polymerization with Metallocene Catalysts," Chem. Rev. 2000, 100, 1253-1345).

[0127] More specifically, it has been found that particular catalysts of the present invention polymerize propylene to isotactic or crystalline polypropylene, forming polymers with novel properties. This polymerization activity for isotactic polypropylene has surprising performance in a solution process. In particular, it has been found that varying the R and Q groups discussed herein allows one to vary the crystallinity index of the crystalline polypropylene formed. In general, reducing the steric bulk of the R<sup>1</sup> group results in a polymer having a lower crystallinity index, such that when Q<sup>1</sup> and Q<sup>5</sup> are both methyl, tacticity may be insufficient to provide a crystalline polymer. Also, the steric bulk of the R<sup>3</sup> and R<sup>7</sup> group can affect the crystallinity index.

[0128] The isotactic polypropylene polymers formed from these catalysts in a solution polymerization process have a crystallinity index of between about 0.35 and about 0.95, more specifically between about 0.65 and 0.95 and in some embodiments preferably above about 0.8, under the polymerization conditions employed. The crystallinity index is determined using FTIR as is known to those of skill in the art and calibrated based on a relative scale. In one embodiment, the crystallinity index value can be determined using commercially available FTIR equipment (such as a Bruker Equinox 55 with an IR Scope II in reflection mode using Pike MappIR software). The crystallinity index is obtained from the ratio of band heights at 995 cm<sup>-1</sup> and 972 cm<sup>-1</sup>. Atactic polypropylene has a ratio of band heights or crystallinity index of 0.2. Greater than 98% isotactic polypropylene has a crystallinity index ratio of greater than 0.95. Generally, the amount of error in crystallinity index measurements is  $\pm 0.05$ . Polymer blends of various compositions show a linear relationship between % isotacticity and crystallinity index. See, for example, J. P. Luongo, *J. Appl. Polym. Sci.*, 3 (1960) 302-309 and T. Sundell, H. Fagerholm, H. Crozier, *Polymer* 37 (1996) 3227-3231, each of which is incorporated herein by reference.

[0129] As those of skill in the art will recognize, isotacticity can also be represented by percent pentads (%mmmm) as determined by  $^{13}\text{C}$  NMR spectroscopy. Proton decoupled  $^{13}\text{C}$  NMR spectroscopy can be performed using commercially available equipment (such as a Bruker 300 MHz at 100°C probe temperature) to determine the degree of tacticity as  
5 %mmmm pentads (for assignment of  $^{13}\text{C}$  signals see the review Brintzinger H.H. *et al.*, *Angew. Chem. Int. Ed. Eng.* 1995, 34, 1143, which is incorporated herein by reference). For example, a 15-30 mg polymer sample is dissolved in a 1:1 mixture of  $\text{C}_2\text{D}_2\text{Cl}_4$  and  $\text{C}_2\text{Cl}_4$  by heating the sample to ca. 100°C. The %mmmm is determined by the ratio of peak integral from 23.5 to 21.5 ppm and peak integral 23.5 to 19 ppm. Proton decoupled  
10  $^{13}\text{C}$  NMR spectroscopy can be also performed to determine the frequency of and nature of stereoerrors and regioerrors.

[0130] In addition, the melting point of the crystalline polypropylene is generally in the range of from about 115°C to about 160°C, more specifically between about 120°C and 155°C, and in some embodiments preferably above about 135°C. Melting points are  
15 determined by differential scanning calorimetry, as is known in the art (see also the example section, herein). Surprisingly, the tacticity level and melting point are relatively level throughout different polymerization temperatures.

[0131] The weight average molecular weight of the crystalline polypropylene according to this application ranges from about 15,000 to about 4,500,000 and for some  
20 embodiments more specifically between about 50,000 to about 500,000 for the polymerization condition of a polymerization temperature at or above about 110°C. The polydispersity of the crystalline polypropylene of this invention ( $M_w/M_n$ ) is generally about 2.5 or lower and in alternative embodiments is between about 2.0 and 3.5.

Molecular weight and polydispersity index is determined according to method known to  
25 those of skill in the art, based, generally on polystyrene standards. As those of skill in the art will recognize, error in molecular weight measurements can range from 10-20%.

[0132] Novel polymers, copolymers or interpolymers may be formed having unique physical and/or melt flow properties. Polymers that can be prepared according to the present invention include propylene copolymers with at least one  $\text{C}_4\text{-C}_{20}$   $\alpha$ -olefin,  
30 particularly 1-butene, 1-hexene, 4-methyl-1-pentene and 1-octene. The copolymers of propylene with at least one  $\text{C}_4\text{-C}_{20}$   $\alpha$ -olefin comprise from about 0.1 wt.% higher olefin to about 60 wt.% higher olefin, more specifically from about 0.2 wt.% higher olefin to about 50 wt.% higher olefin and still more specifically from about 2 wt.% higher olefin

to about 30 wt.% higher olefin. For certain embodiments of this invention, crystalline copolymers include those of propylene and a comonomer selected from the group consisting of ethylene, 1-butene, 1-hexene, and 1-octene comprise from about 0.2 to about 30 wt.% comonomer, more specifically from about 1 to about 20 wt. % comonomer, even more specifically from about 2 to about 15 wt. % comonomer and most specifically from about 5 to about 12 wt. % comonomer.

[0133] The novel polymers (such as isotactic polypropylene) disclosed herein can be employed alone or with other natural or synthetic polymers in a blend. Such other natural or synthetic polymers can be polyethylene (including linear low density polyethylene, low density polyethylene, high density polyethylene, etc.), atactic polypropylene, nylon, EPDM, ethylene-propylene elastomer copolymers, polystyrene (including syndiotactic polystyrene), ethylene-styrene copolymers and terpolymers of ethylene-styrene and other C<sub>3</sub>-C<sub>20</sub> olefins (such as propylene).

[0134] Melt flow rate (MRF) for polypropylene and copolymer of propylene and one or more C<sub>4</sub>-C<sub>20</sub>  $\alpha$ -olefins is measured according to ASTM D-1238, condition L (2.16 kg, 230°C). In some embodiments of this invention, the MFR is in the range of 0.005-1,000, more specifically 0.01-500 and even more specifically 0.1-100. Flex modulus for polypropylene and copolymer of propylene and one or more C<sub>4</sub>-C<sub>20</sub>  $\alpha$ -olefins is measured according to ASTM D-790. In some embodiments of this invention, the flex modulus ranges from 20,000-400,000 psi, more specifically from 20,000-300,000 psi and even more specifically from 100,000-200,000 psi. Notch izod impact for polypropylene and copolymer of propylene and one or more C<sub>4</sub>-C<sub>20</sub>  $\alpha$ -olefins is measured according to ASTM D-256A. In some embodiments of this invention, the notch izod impact ranges from 0.1 to no break in ft-lbs/in.

[0135] The novel polypropylene and copolymer of propylene and one or more C<sub>4</sub>-C<sub>20</sub>  $\alpha$ -olefins disclosed in the present invention are useful for a wide variety of applications, including films (such as blown and cast film, clarity film and multi-layer films), thermoforming (such as cups, plates, trays and containers), injection moulding, blow-moulding, foams (such as structural foams), pipe (such as potable water pipe and high pressure pipe), automotive parts, and other applications that will be evident to those of skill in the art.

[0136] Melt strength (measured in cN) and melt drawability (measured in mm/s) tests are conducted by pulling ("taking-up") strands of the molten polymers or blends at



constant acceleration until breakage occurs. An experimental set-up comprises a capillary rheometer and a Rheotens apparatus as a take-up device. The molten strands are drawn uniaxially to a set of accelerating nips located 100 mm below the die. The force required to uniaxially extend the strands is recorded as a function of the take-up velocity or the nip rolls. In the case of polymer melts exhibiting draw resonance (indicated by the onset of a periodic oscillation of increasing amplitude in the measured force profile), the maximum force and wheel velocity before the onset of draw resonance are taken as the melt strength and melt drawability, respectively. In the absence of draw resonance, the maximum force attained during testing is defined as the melt strength and the velocity at which breakage occurs is defined as the melt drawability. These tests are typically run under the following conditions:

Mass flow rate	1.35 grams/min
Temperature	190°C
Equilibration time at 190°C	10 minutes
Die	20:1 (with entrance angle of approximately 45 degrees)
Capillary length	41.9 mm
Capillary diameter	2.1 mm
Piston diameter	9.54 mm
Piston velocity	0.423 mm/s
Shear rate	33.0 s <sup>-1</sup>
Draw-down distance (die exit to take-up sheels)	100 mm
Cooling conditions	Ambient air
Acceleration	2.4 mm/s <sup>2</sup>

[0137] For some aspects of the present invention the novel polymers are useful to produce foams having improved properties. For foams and other applications requiring melt strength, the MFR is typically in the range of 0.1-10, more specifically in the range of 0.3-3 and most specifically in the range of 0.5-2. The melt strength is typically greater than 5 cN, more specifically greater than 9 cN and most specifically greater than 12 cN. The drawability is typically greater than 15 mm/sec, more specifically greater than 25 mm/sec and most specifically greater than 35 mm/sec.

[0138] In some aspects of the present invention, the novel polymers disclosed herein are useful for a wide variety of applications where certain optical properties are beneficial. Gloss is measured according to ASTM D-1746. Haze is measured according to ASTM

D-1003 and clarity is measured according to ASTM D-2457. The novel polymers disclosed herein in some aspects are films having haze of less than 10%. In addition films having clarity of greater than 91% may be beneficially obtained.

5 **Polymerization Systems**

[0139] Polymerization can be carried out in the Ziegler-Natta or Kaminsky-Sinn methodology, including temperatures of from -100°C to 300°C and pressures from atmospheric to 3000 atmospheres. Suspension, solution, slurry, gas phase or high-pressure polymerization processes may be employed with the catalysts and compounds of this invention. Such processes can be run in a batch, semi-batch or continuous mode. Examples of such processes are well known in the art. A support for the catalyst may be employed, which may be inorganic (such as alumina, magnesium chloride or silica) or organic (such as a polymer or cross-linked polymer). Methods for the preparation of supported catalysts are known in the art. Slurry, suspension, gas phase and high-pressure processes as known to those skilled in the art may also be used with supported catalysts of the invention.

[0140] Other additives that are useful in a polymerization reaction may be employed, such as scavengers, promoters, modifiers and/or chain transfer agents, such as hydrogen, aluminum alkyls and/or silanes.

20 [0141] As discussed herein, catalytic performance can be determined a number of different ways, as those of skill in the art will appreciate. Catalytic performance can be determined by the yield of polymer obtained per mole of metal complex, which in some contexts may be considered to be activity. Table 3 (Figure 3) and Table 4 (Figure 4) display the results of ethylene-1-octene copolymerizations using ancillary ligands of the invention in combination with hafnium and zirconium precursors, respectively. In the case of zirconium, Table 4 illustrates that the yield of copolymer obtained from the experiments is the highest when the zirconium precursor ( $\text{Zr}(\text{CH}_2\text{C}_6\text{H}_5)_4$ ) is employed without the use of an ancillary ligand (Table 4 in Figure 4; Cell A3: 369 mg). This illustrates that the presence of the ancillary ligand may not necessarily enhance the catalytic activity of the zirconium metal center. In the case of hafnium, the yields are unexpected high. In contrast to zirconium, the yield of copolymer obtained when the hafnium precursor ( $\text{Hf}(\text{CH}_2\text{C}_6\text{H}_5)_4$ ) is employed without the use of an ancillary ligand is very low (Table 3 in Figure 3; Cell A3: 47 mg).

[0142] Another measure of catalyst polymerization performance is co-monomer incorporation. As is well known in the art, many ethylene copolymers are prepared using ethylene and at least one other monomer. These copolymers or higher order polymers in some applications require higher amounts of additional co-monomer(s) than have been practical with known catalysts. Since ethylene tends to be the most reactive monomer, obtaining higher co-monomer incorporations is a benefit that is examined for polymerization catalysts. Two useful co-monomers are 1-octene and styrene. This invention offers the possibility of higher incorporation of co-monomers such as 1-octene and styrene. As shown herein, the ethylene/1-octene copolymers obtained from the combination of ancillary ligands and zirconium precursors all possess lower weight % 1-octene values (<11 wt.%) (Table 4 in Figure 4), than the weight % 1-octene values for the ethylene/1-octene copolymers obtained from the combination of ancillary ligands and hafnium precursors.

[0143] The results of the ethylene-1-octene copolymerizations using ancillary ligands of the invention in combination with a hafnium metal precursor are surprising (Table 3 in Figure 3). In contrast to zirconium, the yield of copolymer obtained when the hafnium precursor ( $\text{Hf}(\text{CH}_2\text{C}_6\text{H}_5)_4$ ) is employed without the use of an ancillary ligand is very low (cell A3: 47 mg). Surprisingly, in the presence of certain ancillary ligands, the yields of copolymers obtained are enhanced dramatically relative to cell A3. In addition, the copolymers obtained typically possess higher wt.% 1-octene values relative to the values shown in Table 4. Additionally the wt.% 1-octene values for the copolymers obtained span a wider range (<10 wt.% to 23 wt.%). In contrast to Table 4, the results in Table 3 illustrate the ability of the ancillary ligand to tailor the catalytic performance of the hafnium metal center, both in terms of catalytic activity and the ability to incorporate 1-octene.

[0144] Tables 5 and 5a display the results of ethylene-styrene copolymerizations using ancillary ligands of the invention in combination with hafnium and zirconium precursors. The results in Tables 5 and 5a illustrate that certain combinations of ancillary ligands with hafnium precursors are more productive in the copolymerization of ethylene with styrene than are combinations of the same ancillary ligands with zirconium precursors. Additionally the results illustrate combinations of ancillary ligands with hafnium precursors to produce copolymers with a higher styrene incorporation (wt% styrene by NMR in Table 5 and mol % styrene by FTIR in Table 5a) than the styrene incorporation

in the products produced by the combinations of the same ancillary ligands with zirconium precursors.

[0145] As stated herein, a solution process is specified for certain benefits, with the solution process being run at a temperature above 90°C, more specifically at a temperature above 100°C, further more specifically at a temperature above 110°C and even further more specifically at a temperature above 130°C. Suitable solvents for polymerization are non-coordinating, inert liquids. Examples include straight and branched-chain hydrocarbons such as isobutane, butane, pentane, isopentane, hexane, isohexane, heptane, octane, Isopar-E® and mixtures thereof; cyclic and alicyclic hydrocarbons such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof; perhalogenated hydrocarbons such as perfluorinated C<sub>4-10</sub> alkanes, chlorobenzene, and aromatic and alkylsubstituted aromatic compounds such as benzene, toluene, mesitylene, and xylene. Suitable solvents also include liquid olefins which may act as monomers or comonomers including ethylene, propylene, 1-butene, butadiene, cyclopentene, 1-hexene, 1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1,4-hexadiene, 1-octene, 1-decene, isobutylene, styrene, divinylbenzene, allylbenzene, and vinyltoluene (including all isomers alone or in admixture). Mixtures of the foregoing are also suitable.

[0146] In some embodiments, a solution process is specified for crystalline polypropylene production. The solution process to prepare isotactic polypropylene comprises adding a catalyst and propylene monomer to a reactor and subjecting the contents to polymerization conditions, such that polypropylene is obtained that has a crystallinity index value that does not vary by more than about 0.1, when the temperature of the solution process is varied from a temperature below 90°C to a temperature above 100°C. In some embodiments in this section, the lower temperature is between about 70°C and about 90°C (or between about 75°C and about 95°C or between about 80°C and about 95°C) and the higher temperature is between about 100°C and 110°C (or between about 105°C and about 115°C or between about 100°C and about 115°C). In this context, the solution process can be run at a temperature and pressure that produce a desired product, but generally, the solution process temperature is above 100°C and more specifically above 110°C, while maintaining a high crystallinity index value and high molecular weight. This solution polymerization process also maintains the melting point of the polypropylene, such that it does not vary by more than 10°C, when the

temperature of the solution process is varied from a temperature below 90°C to a temperature above 100°C. In this context, the solution process can be run at a temperature and pressure that produce a desired product, but generally, the solution process temperature is above 100°C and more specifically above 110°C, while  
5 maintaining a melting point above 135°C (and if desired below about 155°C). Also, in this solution process, the process temperature may be at least 110°C while producing polypropylene that has a weight average molecular weight of at least 100,000, more preferably at least about 300,000. In alternative embodiments the stated properties of the polymer are maintained when the temperature of the solution process is varied from a  
10 temperature below about 95°C to a temperature above 105°C or from a temperature below 85°C to a temperature above 105°C. As with the above, these alternative embodiments have a lower temperature limit of about 70°C and an upper temperature limit of about 115°C. The polypropylene properties are made in a process that does not require separation or fractionation of a product into component products (such as  
15 separation of atactic polypropylene from crystalline polypropylene, as is known in the art). Thus, in addition, the properties are measured on the bulk sample. Otherwise, the solution process may be run in accord with methods known to those of skill in the art.

#### **Combinatorial Methodology**

20 [0147] The ligands, metal-ligand complexes and compositions of this invention can be prepared and tested for catalytic activity in one or more of the above reactions in a combinatorial fashion. Combinatorial chemistry generally involves the parallel or rapid serial synthesis and/or screening or characterization of compounds and compositions of matter. U.S. Patent Nos. 5,985,356, 6,030,917 and WO 98/03521, all of which are  
25 incorporated herein by reference, generally disclose combinatorial methods. In this regard, the ligands, metal-ligand complexes or compositions may be prepared and/or tested in rapid serial and/or parallel fashion, e.g., in an array format. When prepared in an array format, ligands, metal-ligand complexes or compositions may be take the form of an array comprising a plurality of compounds wherein each compound can be  
30 characterized by any of the above general formulas (*i.e.*, I, A, II, III, IV, V, VI, VII, VIII, IX, X, XI, XII, XIII or XIV). An array of ligands may be synthesized using the procedures outlined previously. The array may also be of metal precursor compounds, the metal-ligand complexes or compositions characterized by the previously described

formulae and/or description. Typically, each member of the array will have differences so that, for example, a ligand or activator or metal precursor or R group in a first region of the array may be different than the ligand or activator or metal precursor or R group in a second region of the array. Other variables may also differ from region to region in the array.

[0148] In such a combinatorial array, typically each of the plurality of compositions or complexes has a different composition or stoichiometry, and typically each composition or complex is at a selected region on a substrate such that each compound is isolated from the other compositions or complexes. This isolation can take many forms, typically depending on the substrate used. If a flat substrate is used, there may simply be sufficient space between regions so that there cannot be interdiffusion between compositions or complexes. As another example, the substrate can be a microtiter or similar plate having wells so that each composition or complex is in a region separated from other compounds in other regions by a physical barrier. The array may also comprise a parallel reactor or testing chamber.

[0149] The array typically comprises at least 8 compounds, complexes or compositions each having a different chemical formula, meaning that there must be at least one different atom or bond differentiating the members in the array or different ratios of the components referred to herein (with components referring to ligands, metal precursors, activators, group 13 reagents, solvents, monomers, supports, etc.). In other embodiments, there are at least 20 compounds, complexes or compositions on or in the substrate each having a different chemical formula. In still other embodiments, there are at least 40 or 90 or 124 compounds, complexes or compositions on or in the substrate each having a different chemical formula. Because of the manner of forming combinatorial arrays, it may be that each compound, complex or composition may not be worked-up, purified or isolated, and for example, may contain reaction by-products or impurities or unreacted starting materials.

[0150] The catalytic performance of the compounds, complexes or compositions of this invention can be tested in a combinatorial or high throughput fashion. Polymerizations can also be performed in a combinatorial fashion, see, e.g., U.S. Patent Application No. 09/239,223, filed January 29, 1999; U.S. Patent No. 6,306,658 and WO 00/09255, each of which is herein incorporated by reference.

## EXAMPLES

[0151] **General:** All reactions were performed under a purified argon or nitrogen atmosphere in a Vacuum Atmospheres glove box. All solvents used were anhydrous, de-oxygenated and purified according to known techniques. All ligands and metal precursors were prepared according to procedures known to those of skill in the art, e.g., under inert atmosphere conditions, etc. Ethylene/styrene and ethylene/1-octene copolymerizations and propylene polymerizations were carried out in a parallel pressure reactor, which is fully described in pending U.S. Patent Applications Nos. 09/177,170, filed October 22, 1998, 09/239,223, filed January 29, 1999, and WO 00/09255, and U.S. Patent No. 6,306,658 each of which is incorporated herein by reference.

[0152] High temperature Size Exclusion Chromatography was performed using an automated "Rapid GPC" system as described in U.S. Patents 6,175,409, 6,260,407, and 6,294,388 each of which is incorporated herein by reference. In the current apparatus, a series of two 30 cm x 7.5 mm linear columns, with one column containing PLgel 10um, MixB and the other column containing PLgel 5um, MixC (available from Polymer Labs). The GPC system was calibrated using narrow polystyrene standards. The system was operated at a eluent flow rate of 1.5 mL/min and an oven temperature of 160°C. o-dichlorobenzene was used as the eluent. The polymer samples were dissolved 1,2,4-trichlorobenzene at a concentration of about 1 mg/mL. Between 40 µL and 200 µL of a polymer solution were injected into the system. The concentration of the polymer in the eluent was monitored using an evaporative light scattering detector. All of the molecular weight results obtained are relative to linear polystyrene standards.

[0153] The ratio of 1-octene to ethylene incorporated in the ethylene-octene copolymer products was determined by FTIR. FTIR was performed on a Bruker Equinox 55 + IR Scope II in reflection mode using a Pike MappIR accessory with 16 scans. The ratio of 1-octene to ethylene incorporation was represented as the weight % (wt.%) of 1-octene incorporated in the polymer (wt.% 1-octene). Wt.% 1-octene was obtained from ratio of band heights at 1378 cm<sup>-1</sup> and 4335cm<sup>-1</sup>. This method was calibrated using a set of ethylene/1-octene copolymers with a range of known wt.% 1-octene content.

[0154] Crystallinity in polypropylene was determined by FTIR spectroscopy. FTIR spectra of thin films deposited from solution onto gold coated Si wafers are acquired at 4  $\text{cm}^{-1}$  resolution and with 16 scans in reflection-absorption mode on a Bruker Equinox 55 FTIR spectrometer equipped with a Pike MappIR accessory. The height ratio of two  
5 bands at 995  $\text{cm}^{-1}$  (C-H bending and  $\text{CH}_3$  rocking mode from regular crystalline isotactic helices) and 972  $\text{cm}^{-1}$  (coupled C-C stretching and  $\text{CH}_3$  rocking mode, independent of crystallinity) is determined as a measure of isotacticity (as known in the art, see, e.g., J. P. Luongo, *J. Appl. Polym. Sci* 3 (1960) 302-309, and T. Sundell, H. Fagerholm, H. Crozier, *Polymer* 37 (1996) 3227-3231, each of which is incorporated herein by  
10 reference). For blends of atactic and isotactic polypropylene (PP) with 0 – 70% isotactic PP, the IR ratio is proportional to the percentage of isotactic PP. For greater than 98% isotactic PP the ratio is greater than 0.95, for amorphous PP the ratio is 0.2.

[0155] The ratio of styrene to ethylene incorporated in the polymer products, represented as the mol % of styrene incorporated in the polymer (mol% styrene) was determined  
15 using FTIR spectroscopy. The IR spectra (16 scans at 4  $\text{cm}^{-1}$  resolution) analyzed by Partial Least Squares (PLS) analysis with PLSplus/IQ V3.04 for GRAMS/32 (Galactic Industries) software, using the following training set for calibration.

#### Training set

[0156] The analysis based on a training set consisting of 180 spectra of blends of  
20 ethylene-styrene copolymers with known styrene incorporation, and atactic homo-polystyrene. The 16 known copolymers had between 1 and 47 mol% incorporated styrene. The atactic homo-polystyrene content in the blends ranged from 0 to 90% of the total styrene content of the blend. Most blends are prepared from copolymers with up to 20 mol% incorporation. Multiple spectra per blend were included in the training set.

#### Preprocessing of the spectra

[0157] Mean centering; linear baseline correction based on average absorbances at 2074 $\text{cm}^{-1}$  - 2218 $\text{cm}^{-1}$  and 3224 $\text{cm}^{-1}$  - 3465 $\text{cm}^{-1}$ ; thickness correction based on band area from 1483 $\text{cm}^{-1}$  to 1504 $\text{cm}^{-1}$  with baseline from 1389 $\text{cm}^{-1}$  - 1413 $\text{cm}^{-1}$  to 1518 $\text{cm}^{-1}$  - 1527 $\text{cm}^{-1}$ .

#### Analysis

[0158] PLS-1 algorithm; spectral regions 499 $\text{cm}^{-1}$  to 2033 $\text{cm}^{-1}$  and 3577 $\text{cm}^{-1}$  to 4495 $\text{cm}^{-1}$ . Prediction of number ratios of atactic homo-polystyrene to total styrene ( $\propto$  % atactic homo-polystyrene to total styrene) with 10 factors and ethylene to total styrene ( $\propto$



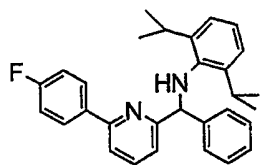
mol% total styrene) with 7 factors and calculation of mol% incorporated styrene from these 2 numbers.

[0159] The ratio of styrene to ethylene incorporated in the polymer products, represented as the weight % (wt. %) of styrene incorporated in the polymer (wt.% styrene) can also  
5 be determined using  $^1\text{H}$  NMR spectroscopy.

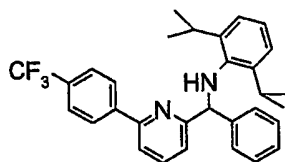
[0160] Differential Scanning Calorimetry (DSC) measurements were performed on a TA instrument DSC 2920 to determine the melting point of polymers. The sample was equilibrated at 200° and held for 4 minutes. The sample was cooled with a rate of 10°C per minute to 55°C where it was held for 10 minutes. The sample was cooled further to -  
10 50°C with a rate of 10°C/min and held at -50°C for 4 minutes. Then, the sample was heated to 200°C at a rate of 1°C/min and data were collected during that heating period.

[0161] Ethylene/isobutylene copolymerizations were carried out in a parallel pressure reactor equipped with a magnetic stirrer hotplate. The ratio of isobutylene to ethylene incorporated in the polymer products, represented as the weight % (wt. %) of isobutylene  
15 incorporated in the polymer (wt.% IB) was determined using  $^1\text{H}$  NMR spectroscopy.

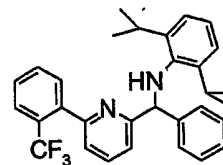
[0162] The following ligands are used in some of these examples:



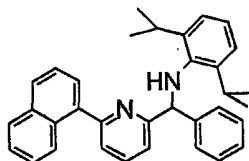
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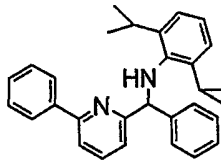
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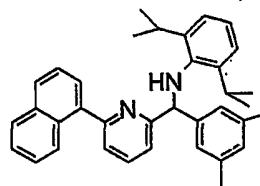
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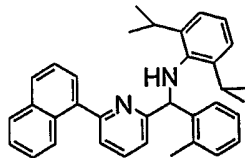
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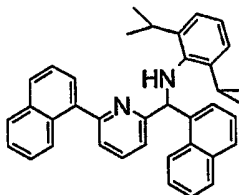
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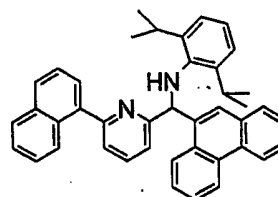
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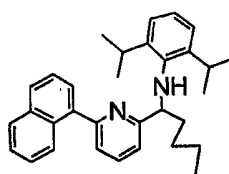
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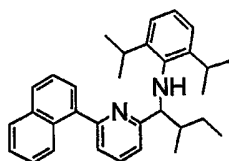
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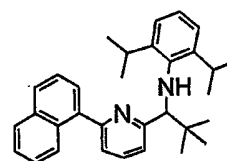
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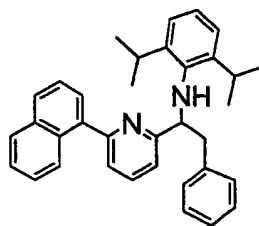
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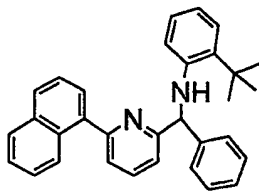
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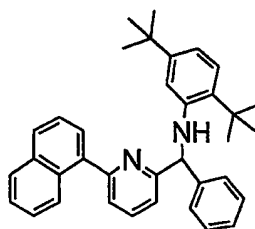
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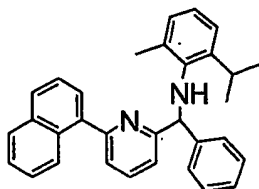
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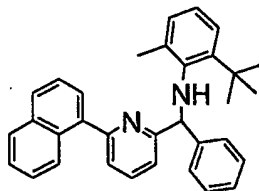
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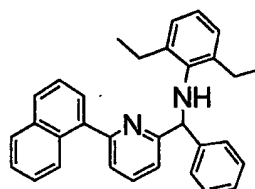
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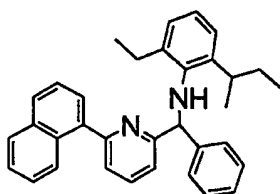
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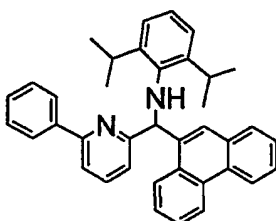
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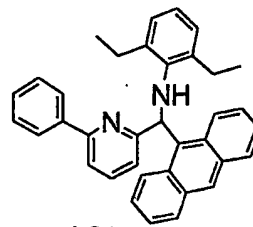
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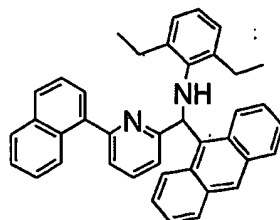
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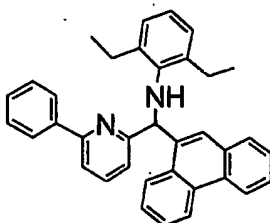
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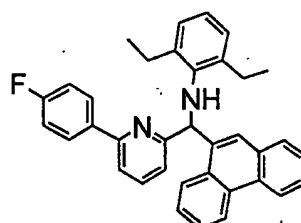
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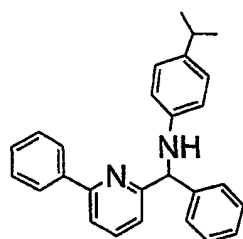
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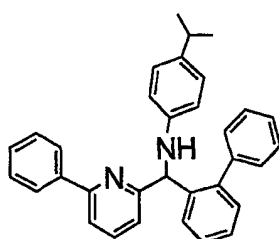
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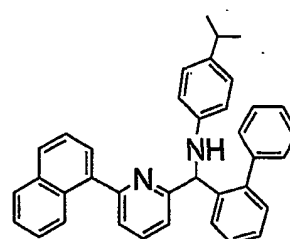
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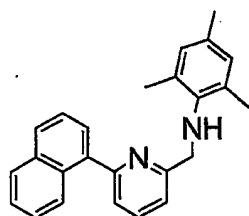
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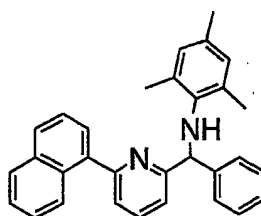
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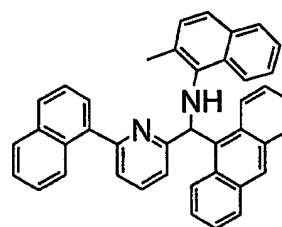
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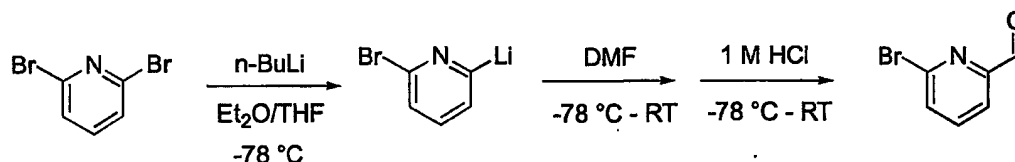


L30

[0163] These ligands were prepared using techniques known to those of skill in the art, for example, using the following general experimental:

5

#### Part A: Synthesis of 2-bromo-6-formylpyridine



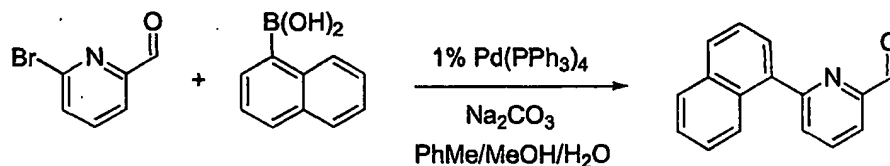
[0164] To a solution of 23.7 g (100 mmol) of 2,6-dibromopyridine in 150 mL of anhydrous, degassed THF cooled to -78 °C was added dropwise under N<sub>2</sub> a solution of 11.0 mL (110 mmol) of 10.0 M <sup>n</sup>BuLi in 150 mL of anhydrous, degassed Et<sub>2</sub>O. After 2 h at -78 °C, 24.2 mL (300 mmol) of anhydrous, degassed DMF was added dropwise with rapid stirring. This solution was stirred at -78 °C for 2 h, then allowed to warm to RT overnight.

[0165] The solution was cooled to -78 °C and 100 mL of 1.0 M aq. HCl was added slowly. The organic phase was separated and the aqueous phase was washed with 3x50 mL Et<sub>2</sub>O. The organic washes were combined and washed with 3x50 mL H<sub>2</sub>O and 3x50 mL brine, then dried over Na<sub>2</sub>SO<sub>4</sub>. The volatiles were removed in vacuo to provide an

orange oil. The oil was triturated with hexanes to give a pale orange solid that was washed with cold pentane and dried under vacuum overnight.

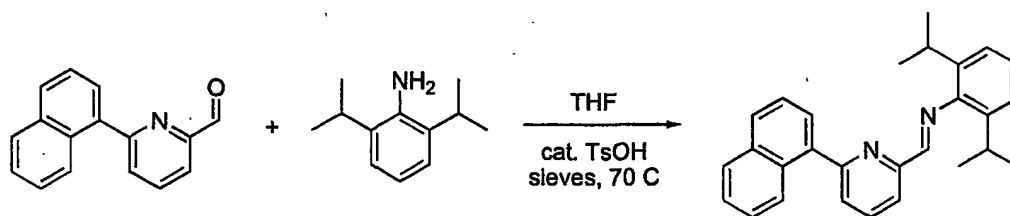
### Part B: Synthesis of 2-formyl-6-naphthylpyridine

5



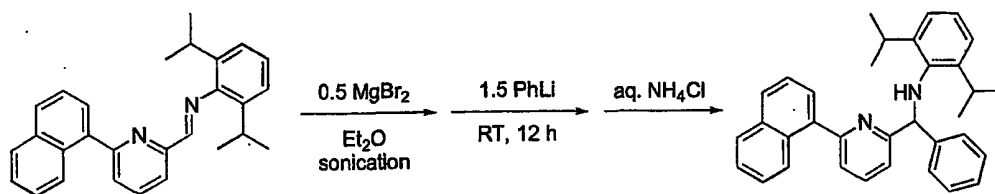
[0166] Naphthylboronic acid (2.06 g, 12 mmol) and Na<sub>2</sub>CO<sub>3</sub> (2.65 g, 25 mmol) were dissolved in 60 mL of degassed 4:1 H<sub>2</sub>O/MeOH. This solution was added via cannula to a solution of 1.86 g (10 mmol) of 2-bromo-6-formylpyridine and 116 mg (0.10 mmol) of Pd(PPh<sub>3</sub>)<sub>4</sub> in 50 mL of degassed toluene. The biphasic solution was vigorously stirred and heated to 70 °C under N<sub>2</sub> for 4 h. On cooling to RT, the organic phase was separated and washed with 3x25 mL of Et<sub>2</sub>O. The combined organic extracts were washed with 3x25 mL of H<sub>2</sub>O and 1x20 mL of brine and dried over Na<sub>2</sub>SO<sub>4</sub>. After removing the volatiles in vacuo, the resultant brown oil was chromatographed on silica with 0 – 50% hexanes/CH<sub>2</sub>Cl<sub>2</sub>. The early fractions contained naphthalene and binaphthyl and were discarded. The remaining fractions were combined and the volatiles were removed to provide 2-formyl-6-naphthylpyridine as a white solid.

### 20 Part C: Synthesis of 6-naphthylpyridine-2-(2,6-diisopropylphenyl)imine



[0167] A solution of 1.17 g (0.5 mmol) of 2-formyl-6-naphthylpyridine and 0.98 g (0.55 mmol) of 2,6-diisopropylaniline in 50 mL of anhydrous THF containing 3 Å sieves and a catalytic amount of TsOH was heated to reflux under N<sub>2</sub> for 12 h. After filtration and removal of the volatiles in vacuo, the crude material was passed through a 4x6 cm plug of neutral alumina with 1:1 hexanes/ CH<sub>2</sub>Cl<sub>2</sub> eluent. Removal of the volatiles provided 6-naphthylpyridine-2-(2,6-diisopropylphenyl)imine as yellow crystals.

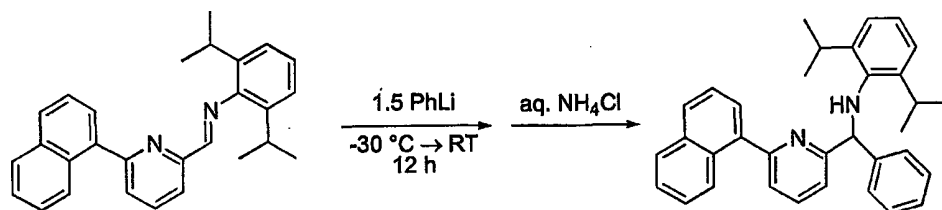
**Part D: Synthesis of (6-naphthyl-2-pyridyl)-N-(2,6-diisopropylphenyl)benzylamine (Ligand L4)**



5

**Synthesis With MgBr<sub>2</sub> Precomplexation:**

[0168] To a well-stirred slurry of powdered MgBr<sub>2</sub> (184 mg, 1 mmol) in 2 mL of anhydrous, degassed Et<sub>2</sub>O was added under N<sub>2</sub> a solution of 6-naphthylpyridine-2-(2,6-diisopropylphenyl)imine (392 mg, 1 mmol) in 2 mL of Et<sub>2</sub>O. The mixture was sonicated until the yellow color of the imine dissipated and a free-flowing pale yellow powder was formed. To this suspension was added with vigorous stirring a solution of phenyllithium (833 uL of 1.8 M in cyclohexane, 1.5 mmol). After stirring at RT for 12 h, the reaction was quenched with aq. NH<sub>4</sub>Cl. The organic layer was separated, washed with brine and H<sub>2</sub>O, then dried over Na<sub>2</sub>SO<sub>4</sub>. Following chromatography (silica gel, 3% THF/hexanes), the product was isolated as a colorless oil.



20

**Synthesis Without MgBr<sub>2</sub> Precomplexation:**

[0169] To a solution of 6-naphthylpyridine-2-(2,6-diisopropylphenyl)imine (392 mg, 1 mmol) in 5 mL of anhydrous, degassed Et<sub>2</sub>O cooled to -30 °C under N<sub>2</sub> was added a solution of phenyllithium (833 uL of 1.8 M in cyclohexane, 1.5 mmol). After warming to RT over 1 h. the soln. was stirred at RT for 12 h. The reaction was then quenched with aq. NH<sub>4</sub>Cl, and worked-up as above.

[0170] This same procedure is followed for the different ligands, but with the following different starting materials for the different ligands:

In part B:

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